An Accurate Equation-of-State Model for Chemically Reactive C-N-O Systems

Sergey B. Victorov, Sergey A. Gubin, Irina V. Maklashova, Yulia A. Bogdanova

Moscow Engineering Physics Institute (State University),
31, Kashirskoe chaussee, Moscow 115409, Russia

1 Introduction

The knowledge of thermodynamic properties of chemically reactive systems composed of C, N, and O atoms is necessary in solving a variety of practical problems in many fields of science. In particular, high-pressure high-temperature thermodynamic data on multicomponent C-N-O systems are needed in the chemistry and physics of shocks and detonations. The development of reliable equation of state (EOS) models for such systems is of great theoretical and practical interest.

In this work, we present a new accurate multiphase EOS model for chemically reactive N-O, C-O, C-N, and C-N-O systems, which was recently incorporated into the thermochemical TDS code and is applicable over a wide range of temperatures and densities covering both the high-pressure area (up to tens of gigapascals) and the region of moderate pressures ($P < 1$ GPa). This model consists of a theoretical EOS for a multicomponent gaseous (fluid) phase and a thermodynamically consistent semi-empirical model for the solid and liquid nanoparticles of graphite and diamond. Thus, the thermodynamic computations based on the model presented allow one to obtain the data on thermodynamic properties and the chemical and phase composition of the system being investigated taking into account the possibility of formation of the diamond or graphite nanoparticles in the product mixture. The model can be applied to predicting and analyzing a complicated multi-front structure of detonation wave for explosives whose detonation products undergo nanocarbon phase transitions. The examples given in this work show that our model provides accurate thermodynamic description of the states of the N-O, C-O, C-N, and C-N-O systems realizable in static, dynamic (shock wave), and detonation experiments. We also present the results of comparisons to the predictions of EOS models used in other known thermochemical codes (CHEQ, the code of Jones and Zerilli, CARTE, Cheetah).

2 Equations of state

In this work, the multicomponent gaseous (fluid) phase of the products is supposed to contain any combination of the following molecules and atoms: N_2, N, O_2, O, NO, N_2O, NO_2, CO_2, and CO. It is assumed that molecules i and j of the gaseous phase interact via a spherically symmetric α-exponential-6 (Exp-6) potential $\varphi_{ij}(r)$, where r is the intermolecular separation. Such potentials with the three constant parameters provide realistic description of the intermolecular forces in dense gases composed of non-polar or almost non-polar molecules and are especially suitable under high-pressure high-temperature conditions relevant to detonation and shock wave problems.

To calculate the thermodynamic properties of gaseous mixtures, we use an improved van der Waals one-fluid (vdW1f) model, which assumes a mixture of chemical species, interacting via Exp-6 potentials, to be a hypothetical one-component fluid with an effective Exp-6 potential whose parameters are composition-

Correspondence to : sb_victorov@mail.ru

dependent. The reliability of vdW1f in predicting the excess thermodynamic parameters of multicomponent fluids has been shown by Ree and confirmed by our results.

A multicomponent EOS based on vdW1f requires for an accurate one-component Exp-6 EOS model. In this work, we use a new version [1] of the KLRR perturbation theory that improves the accuracy of computing the thermodynamic parameters of the Exp-6 fluid at high densities and especially for stiff potentials ($\alpha > 14$) in comparison with the original and Byers-Brown and Horton's versions of KLRR. Our comparisons show that the multicomponent EOS obtained reproduces the results of Monte Carlo simulations for Exp-6 mixtures more accurately than the models based on vdW1f and MCRSR (CHEQ, CARTE) or on vdW1f and HMSA (Cheetah).

We present the values of the Exp-6 parameters determined by matching experimental Hugoniot data and available results of static experiments for the region of moderate pressures and temperatures. The unlike-pair Exp-6 parameters are additive, i.e. they follow the Lorentz–Berthelot combination rules ($k_{ij} = l_{ij} = m_{ij} = 1$), for all pairs except for CO_2–O, for which we found the best-fitting value of $k_{CO2-O} = 0.91$.

The model of nanocarbon used in this work involves the semi-empirical EOSs for the solid and liquid nanoparticles of graphite and diamond [2]. The EOSs are based on an accurate multiphase model of the bulk carbon and have correction terms that allow one to take into account the effect of the small size of carbon particles on their thermodynamics. The correction terms represent approximate expressions for the surface energy of nanoparticles that depend on the material and the size and shape of the particles. The enthalpy and entropy of the nano-size material are calculated by adding the correction terms to the corresponding quantities of the same bulk material. The present model shifts the nano-size solid graphite – solid diamond phase equilibrium line upward in pressure relative to the bulk graphite–diamond equilibrium line (see Fig. 1), so that in a limited region of temperatures and pressures between those two lines, the graphite nanoparticles remain thermodynamically stable whereas the bulk graphite is unstable under the same conditions. As seen in Fig. 1, the model also shifts the line of nanocarbon melting downward in temperature. The determined absolute values of the heat of formation of graphite and diamond are consistent with the available measurements for the heat of formation of nanocarbon recovered from detonation calorimetry experiments.

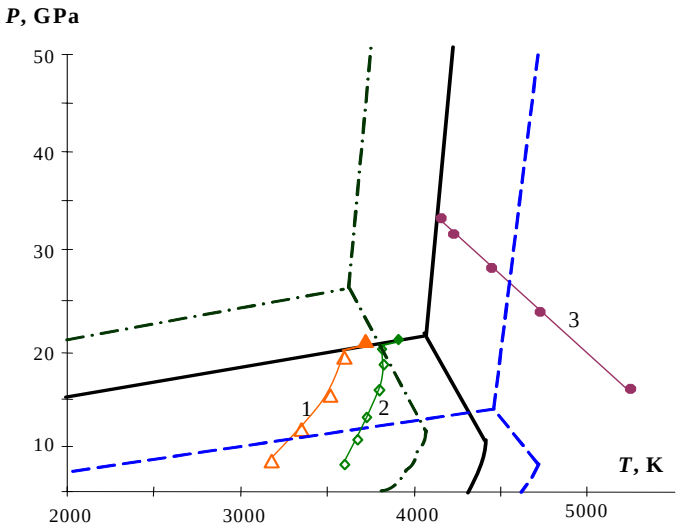

Fig. 1. The phase diagrams of the carbon computed with our model. The dotted (blue) lines are the phase diagram of the bulk carbon. The solid (black) lines are the phase diagram of the detonation nanocarbon (the particle size is 5 nm). The dash-dot lines are the phase diagram of the nanocarbon with the particle size of 2 nm. The symbols and lines labelled "1", "2", and "3" show the computed thermodynamic states of the detonation products of three explosives at different charge densities (1 – TNT, 2 – HNS, 3 – BTF).

3 Results

Using the TDS code, we applied the multiphase EOS model presented to compute the thermodynamic properties of several N-O, C-O, C-N, and C-N-O systems over a wide range of pressures and temperatures. The results are in good agreement with experimental Hugoniot data (Fig. 2), static measurements (Fig. 3), and detonation experiments (Table 1). The detonation experiments were not used to calibrate the Exp-6 parameters of our model. Thus, good agreement with the measured detonation properties of explosives confirms the reliability of the model presented. We also carried out a series of TDS computations with other EOSs of the gaseous phase, namely, the semi-empirical BKWR and BKWC EOSs and the theoretical Exp-6 models from other aforementioned thermochemical codes. The comparisons showed that our model yields much more reliable results than BKW-based EOSs and provides more accurate agreement with experiments than theoretical models of other authors. Among the examined EOSs of other authors, the best results were obtained with the model used in the Cheetah code with the potential parameters determined in the recent work [3]. However, in comparison with the predictions of our model, the computations with the model [3] yielded somewhat less accurate results in reproducing the data of shock wave and static experiments and, as a result, of detonation experiments as well.

4 Conclusion

We developed an accurate EOS model for multiphase and multicomponent chemically reactive systems that allows for reliably computing the thermodynamic properties and chemical composition of C-N-O systems and their N-O, C-O, and C-N subsets over a wide range of pressures and temperatures. The TDS code with the model presented can be applied to solving a variety of problems in many fields of science including the chemistry and physics of shock waves and detonations. In particular, the reliability of our model allows one to use it for predicting the detonation parameters of new explosives that are not studied experimentally. Among possible applications of the model, we note an opportunity of predicting and analyzing a complicated multi-front structure of detonation wave for explosives whose detonation products undergo nanocarbon phase transitions. Such possibility was recently shown by Victorov and Gubin. The model is also suitable for the region of moderate pressures and temperatures.

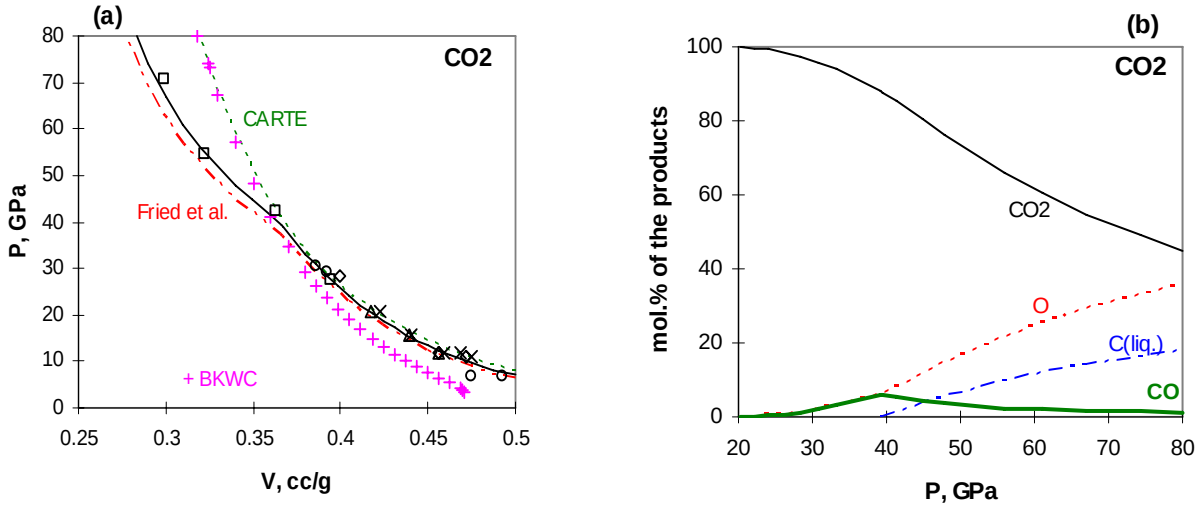

Fig. 2a. The measured (symbols except for "+") and computed (lines and symbols "+") Hugoniots of initially liquid CO_2. The solid line corresponds to the computations based on our model.

Fig. 2b. The chemical composition of the products along the Hugoniot of CO_2 computed with our model.

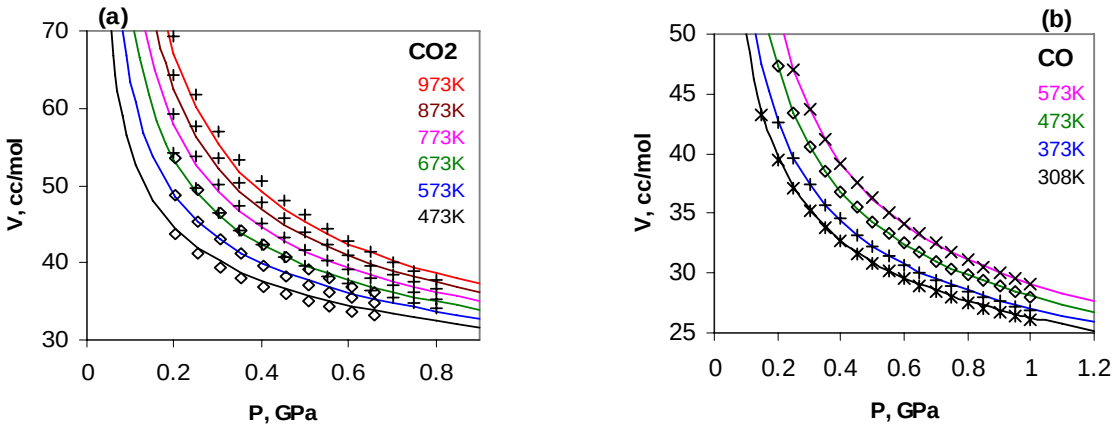

Fig. 3. The isotherms of CO_2 (*a*) and CO (*b*) measured (symbols) and computed (lines) with our model.

Table 2. The results*) of comparisons of the measured detonation parameters to those computed with the model presented in this work ("TDS") and with the models from other thermochemical codes

Explosive	TDS	Cheetah	CARTE	Jones, Zerilli	CHEQ	BKWR	BKWC
NO	+	–	+	+	–	+	+/–
C_3N_{12}	+	+/–	–	+/–	+	–	–
CN_4O_8	+	+	+	+	–	–	–
$C_2N_6O_{12}$	+	+/–	+	+	–	–	+
$C_6N_6O_{12}$	+	+	+/–	–	–	–	–
$C_6N_{12}O_6$	+	+	+	+	–	–	+/–
$C_4N_8O_8$	+	+/–	–	–	–	–	+

*) The symbols "+", "+/–", and "–" mean good (within the experimental uncertainties), satisfactory, and poor agreement with experiments, respectively.

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