

# **A THERMOCHEMICAL CODE (TDS) FOR THERMODYNAMIC CALCULATIONS OF COMPLEX CHEMICAL SYSTEMS**

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There are many situations where accurate calculation of thermodynamic properties of complex chemical systems, including multiphase and multicomponent mixtures of gases, liquids, solids, and fluids, is desirable. In particular, such calculations are needed in the high pressure areas which are of interest in geophysics, in astrophysics (e.g., planetary interiors), and in other fields of science. In the chemistry and physics of shocks and detonation the knowledge of thermodynamic properties of the detonation products allows one to solve a series of practically important problems, including evaluation of high explosive (HE) performance, generation of HE equation of state (EOS) data for hydrodynamic simulations, and so on.

We have developed a thermochemical code (TDS) which is designed to perform thermodynamic calculations of compositions and properties of complex chemically reacting or inert systems described by various equations of state under conditions of equilibrium and non-equilibrium. Initial reactants, as well as products, form multicomponent and/or multiphase systems that include a wide variety of elements and compounds. The thermodynamic computation is based on the fundamental Gibbs extremum principle. TDS solves thermodynamic equations for product species and unknown thermodynamic parameters of the system in chemical equilibrium. The program searches for conditional extremum of multivariable function, by solving a system of non-linear equations, for a given chemical system (i.e., a number of chemical elements, reaction products, etc.). The TDS code can be used to solve the basic (*TV*, *TP*, *UV*, *HP*, *SV*, and *SP*) thermodynamic problems as well as to determine thermodynamic states and compositions of products in stationary gas flows. In particular, one can run the TDS code to simulate detonation in gaseous and condensed explosives, shock waves in various media.

Computations can be performed both under the condition of complete equilibrium and under prescribed chemical, thermal, or mechanical non-equilibrium conditions. In chemically

non-equilibrium problems, frozen concentrations of one or more product species are preset as initial data. For the case of thermal non-equilibrium, products may include phases with different temperatures. For the case of a mechanical non-equilibrium, which may occur in stationary gas flows, phases may have different velocities. The TDS code has a wide range of applications because it allows a user to perform non-equilibrium calculations. In particular, chemical non-equilibrium computations can be performed to effectively simulate real low-temperature processes in which products have not reached the equilibrium state.

TDS treats the following types of products: multicomponent and/or multiphase chemical systems, including solid and liquid components; systems with fluid phase separation (gas–gas equilibria); ionized species; nanodisperse condensed systems. Unlike other well-known thermochemical codes, that require the presence of a gaseous phase in products, TDS can treat the entire chemical system composed only of condensed species and successfully solves the problems with the simultaneous presence of gases and a high content of condensed species. The code calculates combustion characteristics of any fuel, including pollutant characteristics; equilibrium characteristics of vapor–liquid systems; phase diagrams for single- and multicomponent systems; characteristics of basic processes for various engines, power plants, and chemical apparatus; synthesis of high-melting compounds; and properties of nanodispersed substances.

TDS incorporates databanks of caloric properties of more than 2000 individual species and databases containing the parameters of various theoretical and semi-empirical thermal EOSs for gaseous and condensed phases. In computations of multiphase chemical systems, each phase is described by a specific thermal EOS. For example, condensed phases can be described by Cowan's EOS or several modifications of the Gruneisen EOS. Any solid or liquid phase, whose high-density properties are practically unknown, can be treated by the simplest EOS of an incompressible condensed substance.

The thermodynamic properties of real gaseous systems can be described by EOSs of several types. A rarefied gaseous system is described by the equation of state of a perfect gas. Fluids (gaseous) systems under high density are described by the Becker–Kistiakowski–Wilson (BKW) equation or several theoretical models based on intermolecular potentials and accurate thermodynamic perturbation theories or integral equations for pair distribution functions.

The TDS-code package also includes theoretical based EOS derived by using the thermodynamic perturbation theory in KLRR form [2 ] and the integral equation method HMSA [3] for the radial distribution function, based on the Exp-6 intermolecular interaction potential. Since the Exp-6 potential is quite realistic and the underlying physical theories are well substantiated, these EOS can be used to obtain reliable predictions of fluid properties in broad temperature and pressure ranges.

These theory was employed in form of Byers-Brown's analytical representation [4]. We have extended the original Byers-Brown's THEOSTAR expressions to the case that all the Exp-6 parameters (or any of them) may depend on temperature. A convenient acronym for this extended version is THEOSTAR-T. The TDS code supports the THEOSTAR-T model in its extended form. A widely used form of the Exp-6 potential with the temperature-dependent well depth has been incorporated into the TDS code as a standard tool.

The TDS code is PC-based program. It has a multiple-window user interface, which makes it much easier to run the code, particularly for users that are familiar with the Microsoft Excel spreadsheet (since the TDS and Excel shells are outwardly very similar). TDS provides the user with online help, warnings, and error messages. The TDS code can be effectively used as an up-to-date, versatile toolkit for analyzing diverse physical and chemical processes and thermodynamic properties of real chemical compounds, and also as educational tool for technical universities.

In particular, the TDS code allows one to compute high explosive performances including the parameters of the Chapman–Jouguet (CJ) detonation. In solving the detonation problem, the code uses a special technique that guarantees correct determination of the phase composition of detonation products even for the explosives, whose reactive Hugoniot have discontinuities in thermodynamic derivatives due to phase transitions.

To demonstrate the predictive ability of TDS-code we calculated detonation properties of high explosives using theoretical EOS of fluid detonation products, whose parameters were determined without the use of experimental HE detonation properties.

An EOS based on the KLRR perturbation theory [2], theory was employed in present work. This theory are equations for pair distribution function of molecules, it compares well with Monte Carlo simulation data for different types of intermolecular potentials. The exponential-six potential model (Exp-6 or the modified Buckingham potential) was used to

describe intermolecular interactions. Multicomponent fluid mixtures of detonation products were considered in the framework of the effective one-component model (the improved van der Waals one-fluid model vdW1f) suggested by F. Ree [5]. The Exp-6 parameters for  $N_2$ , N,  $O_2$ , O, NO,  $CO_2$ , and CO molecules have been determined. It allows us to calculate thermodynamic properties of fluid mixtures containing C, N, and O atoms. The potential parameters for like-pairs of molecules have been obtained to accurately reproduce available experimental results on static and dynamic compression. Detonation properties of HE were not used in the determination of the intermolecular potentials. The obtained Exp-6 parameters are listed in Table 1. The potential parameters for unlike pairs of molecules are assumed to follow the Lorentz-Berthelot combination rules.

The detonation products of typical HE may contain graphite or diamond nanoparticles. Therefore, there is a need to determine the EOS of these phases of solid carbon. In this work we use the Gruneisen EOS for graphite and diamond [6] with our correction that takes into account the influence of the small size of carbon particles on their thermodynamic properties.

The EOS correction consists of the use of both the increased heats of formation (4.8 kcal/mol for the graphite and 6.75 kcal/mol for the diamond instead of the standard values of 0 and 0.453 kcal/mol, respectively) and the slightly changed densities at the standard (room) state ( $2.32 \text{ g/cm}^3$  for the graphite and  $3.3 \text{ g/cm}^3$  for the diamond instead of the standard values of 2.27 and  $3.515 \text{ g/cm}^3$ ). The specified values of the heat of formation and of the standard state density of carbon nanoparticles were determined to provide the best agreement between the calculated and measured detonation parameters for a series of carbon-rich explosives. For example, such graphite and diamond EOS lead to a break in the slope of the TNT detonation velocity vs. initial TNT density due to the graphite–diamond transition that occurs at  $\rho_0 = 1.55 \text{ g/cm}^3$  in exact agreement with the experiments.

Although measured detonation properties of explosives were not used for the calibration of the potentials, the computed CJ parameters are in excellent agreement with the experiments (see Table 2). Some experiments results are in [7]. The same CJ parameters were also calculated with the BKWC EOS [7] which is one of the last semi-empirical EOS of detonation products. One can see, that the BKWC predictions are more poor than ones obtained with the KLRR theory.

All calculations based on both theoretical and semi-empirical EOS are done by our thermodynamic code TDS. Thus, the TDS code is the convenient computer tool to perform thermodynamic properties of complex chemical systems and fluid mixtures.

**Table 1.** The Exp-6 parameters for like-pairs of molecules that have been obtained in this work

( $k_B$  - Boltzman constant)

Molecules	$\epsilon_0/k_B$ , K	$r_m$ , E	$\alpha$	Molecules	$\epsilon_0/k_B$ , K	$r_m$ , E	$\alpha$
N <sub>2</sub> – N <sub>2</sub>	100.6	4.25	12.3	NO – NO	182.9	3.70	13.0
N – N	120.0	2.65	10.4	CO <sub>2</sub> – CO <sub>2</sub>	247.2	4.26	13.4
O <sub>2</sub> – O <sub>2</sub>	96.2	3.79	14.7	CO – CO	99.5	4.13	14.0
O – O	277.0	2.57	11.5				

**Table 2**

Measured and predicted detonation properties of explosives

HE $\Delta H_f$ , kcal/mol; $\rho_0$ , g/cm <sup>3</sup>	$D$ , km/s experiment klrr-c / bkwc / bkwr	$P_{CJ}$ , GPa experiment klrr-c / bkwc / bkwr	$T_{CJ}$ , K experiment klrr-c / bkwc / bkwr
NO	5.62	10	–
21.0; 1.30	5.61 / 5.84 / 5.77	9.9 / 10.5 / 11.2	3058 / 3414 / 2891
C <sub>3</sub> N <sub>12</sub>	5.60	–	–
218.6; 1.15	5.65 / 5.96 / 5.98	8.9 / 9.7 / 10.5	3954 / 4072 / 3628
CN <sub>4</sub> O <sub>8</sub> (TNM)	6.45	15.5	–
8.8; 1.65	6.46 / 6.26 / 6.18	15.1 / 13.8 / 14.8	2222 / 2651 / 2112
C <sub>2</sub> N <sub>6</sub> O <sub>12</sub>	7.58	–	–
28.6; 1.86	7.59 / 7.48 / 7.20	24.0 / 22.0 / 22.6	2509 / 3154 / 2463
C <sub>6</sub> N <sub>6</sub> O <sub>12</sub> (HNB)	9.34	43	–
15.7; 1.965	9.41 / 9.16 / 8.83	39.3 / 37.0 / 37.8	4942 / 5297 / 4422

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