The equilibrium equation of state of gas mixture with the detailed considering of the chemical composition

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Thermodynamic model with a frozen chemical composition

$h_i(T)$ – The enthalpy of 1 mole of matter versus temperature in the "standard state" ($p_0 = 101325$ Pa).

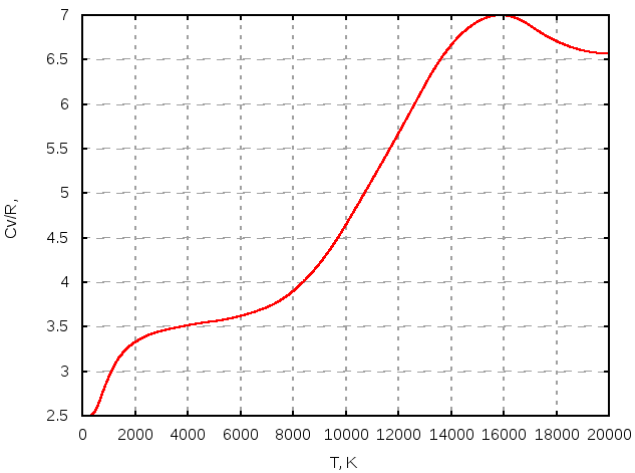
$$H(T,p) = \begin{bmatrix} \sum_i \nu_i h_i(T) \\ \sum_i \nu_i h_i(T) + (p - p_0) V_{cond\,i} \end{bmatrix}$$ – полная энтальпия системы.

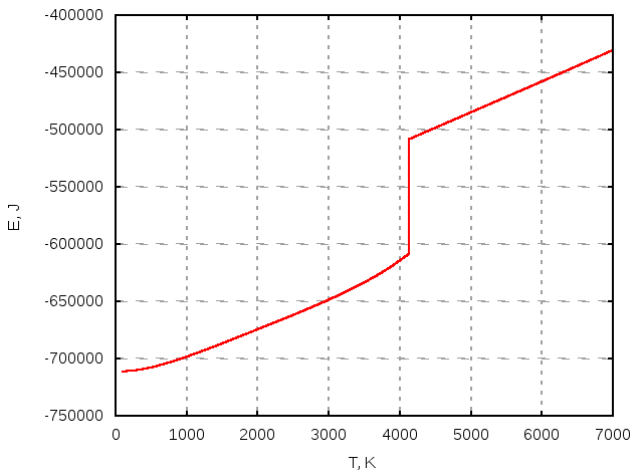
$$E(T) = \begin{bmatrix} \sum_i \nu_i (h_i(T) - RT) \\ \sum_i \nu_i h_i(T) - p_0 V_{cond\,i} \end{bmatrix}$$ – Total energy of the system.

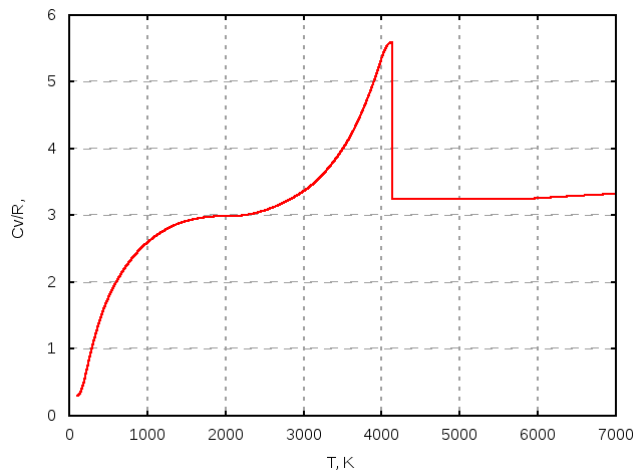
The density of the condensed phase is assumed to be constant.

$p = \nu_{gase} RT / V_{gase}$ – давление, где $V_{gase} = V - \sum_i V_{cond\,i}$.

$c_v = \left(\frac{\partial E}{\partial T}\right)_V$, $c_p = \left(\frac{\partial H}{\partial T}\right)_p$, $\gamma_f = c_p / c_v$, $c_f = (\gamma_f p / rho)^{1/2}$.







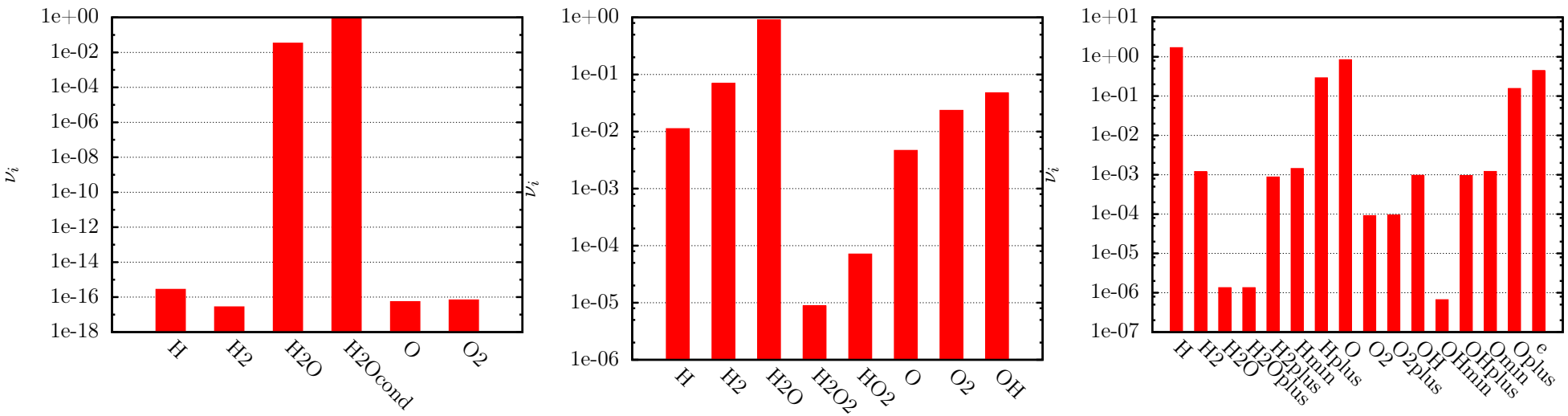
The heat capacity of nitrogen (N_2), the internal energy and heat capacity of condensed carbon (graphite, liquid carbon).

The thermodynamic model of reacting rarefied gases

$$F_i(N_i, V, T) = -kT\left[\ln\left(\left(f_i(T)Ve^{-e^i/kT}\right)^{N_i}/N_i!\right)\right], F(V,T) = \sum F_i(N_i, V, T).$$

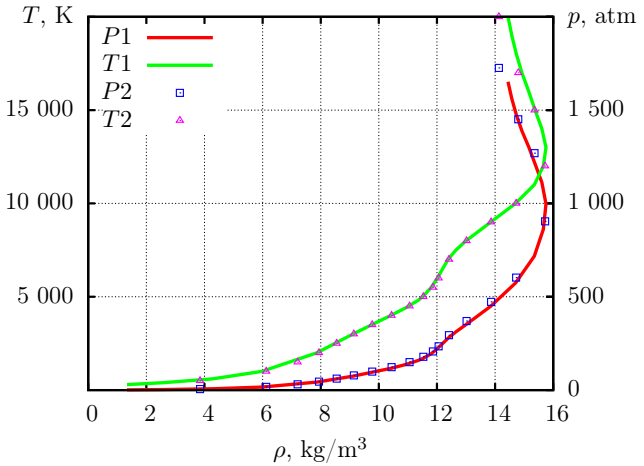
$V,\ T = const$ min F.

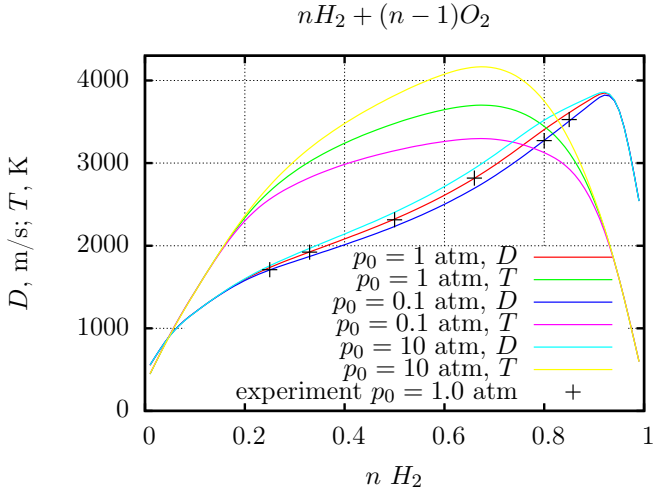
- V.P. Glushko, D. Stall.
- NIST Chemistry WebBook. Thermodynamic data for 7000 compounds.
- NASA online CEA. Thermodynamic and gas dynamic calculations for 2000 compounds.

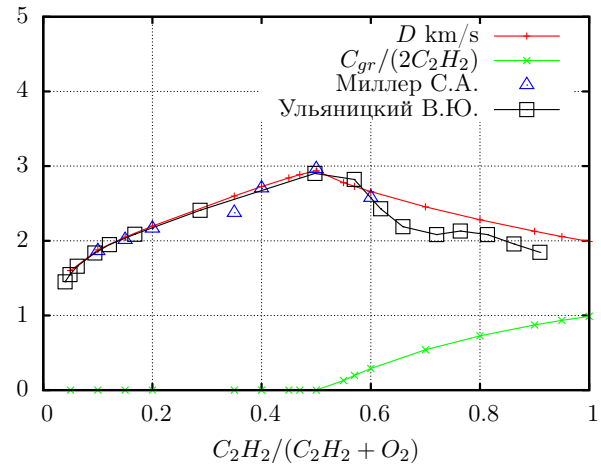


Equilibrium chemical concentrations of a mixture of gases with a composition of $2H + O$ (water) at a temperature of 300, 3000 and 20 000 K. The density is 1 kg/m^3.

Testing for gas-dynamic flows: shock and detonation waves





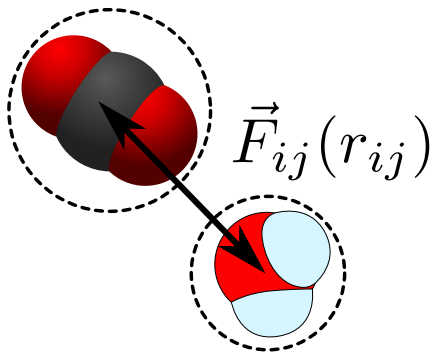


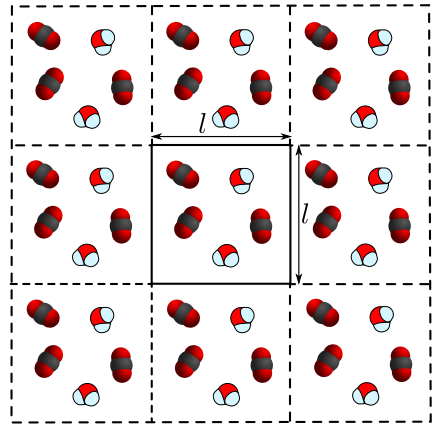
Shock wave in the atmosphere. Detonation of mixtures of hydrogen and acetylene with oxygen ($D = u + c$).

www.ancient.hydro.nsc.ru/chem. Shock and detonation waves, gas suspension, the possibility of forming gas components: Ar, Ar^+, C2, C2H2, C2H4, C2H6, $C2^-$, C2N2, $C2^+$, C3, C3H8, C4, C4H10, C5, Ccond, C, CH4, CH, C^-, CN, CO2, $CO2^+$, CO, CO^+, C^+, e, H2, H2O2, H2Ocond, H2O, $H2O^+$, $H2^+$, $H3O^+$, $H3^+$, H, He, He^+, H^-, HO2, $HO2^-$, H^+, N2, N2O3, N2O4, N2O5, N2O, $N2^+$, N3, N, NH3, NO2, $NO2^-$, $NO3^-$, NO, NO^+, N^+, O2, $O2^-$, $O2^+$, O3, O, OH, OH^-, OH^+, O^-, O^+, Si2C, Si2, Si3, SiC2, SiCcond, SiC, SiCgase, SiCliq, Sicond, Si, Sigase, SiH2, SiH3, SiH4, SiH, Siliq, SiN, SiO2cond, SiO2, SiO2gase, SiO2liq, SiO, Si^+;

and condensed phases C, H_2O, SiO_2, Fe, FeO, Fe_2O_3, Fe_3O_4, FeS, FeS_2.

A mixture of reacting dense gases. The Monte Carlo Method





The free energy of internal degrees of freedom: rotation, oscillations, and electronic excitations depends only on temperature.
$W = \prod_i \left((f_i(T)V)^{N_i}/N_i!\right) e^{-U(\vec{r}_1,\ldots\vec{r}_l)/kT}$, $W_{p,q} \sim W_q/W_p$.

- Change in chemical composition according to the balance of the reaction.
- Displacement of particles: random or according to the laws of mechanics.
- Acceptance or rejection of a new state.

$U = 4\varepsilon\left(\left(\frac{b}{r}\right)^{12} - \left(\frac{b}{r}\right)^{6}\right)$ – the Lennard-Jones potential,

$U_{exp-6} = \frac{\varepsilon}{1-6/\alpha}\left(\left(\frac{6}{\alpha}\right)\exp\left[\alpha\left(1-\frac{r}{b}\right)\right] - \left(\frac{b}{r}\right)^{6}\right)$ – exp-6 potential.

C, C_{cond}, O, O_2, H, H_2, N, N_2, NO, CO, CO_2, H_2O, OH, CH_4, NH_3.

Calculation of thermodynamic parameters.

$PV = NkT - 1/6\sum_{i=1}^{N}\sum_{j\neq i}^{\infty} r_{ij}F(r_{ij})$, $E = 1/2\sum_{i=1}^{N}\sum_{j\neq i}^{\infty} U(r_{ij}) + \sum_{i=1}^{N} N_i e_i(T)$.

Calculation of the thermodynamic characteristics of the system

Calculated by the Monte Carlo method: $p(\rho, T)$, $E(\rho, T)$.

Calculated numerically: $\left(\frac{\partial p}{\partial \rho}\right)_T$, $\left(\frac{\partial p}{\partial T}\right)_\rho$, $\left(\frac{\partial E}{\partial \rho}\right)_T$, $\left(\frac{\partial E}{\partial T}\right)_\rho$.

Calculated through the appropriate thermodynamic relationships:

$$c_v = \left(\frac{\partial E}{\partial T}\right)_\rho,$$

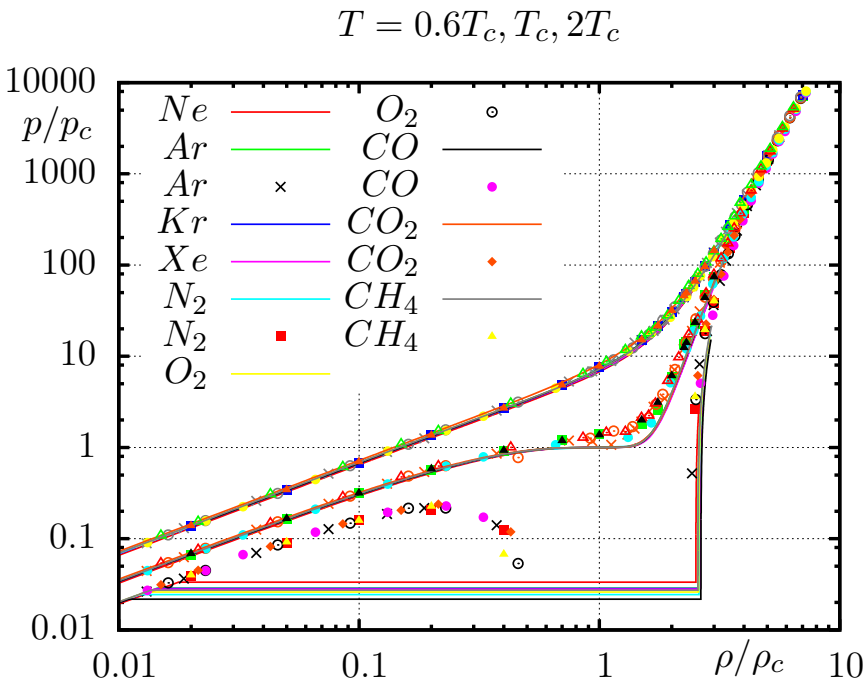
$$c_p = c_v + \left(\frac{pm}{\rho^2} - \left(\frac{\partial E}{\partial \rho}\right)_T\right)\left(\frac{\partial p}{\partial T}\right)_\rho \Big/ \left(\frac{\partial p}{\partial \rho}\right)_T,$$

$$c_{sound} = \left(\frac{\partial p}{\partial \rho}\right)_S^{1/2} = \left(\left(\frac{\partial p}{\partial \rho}\right)_T \frac{c_p}{c_v}\right)^{1/2},$$

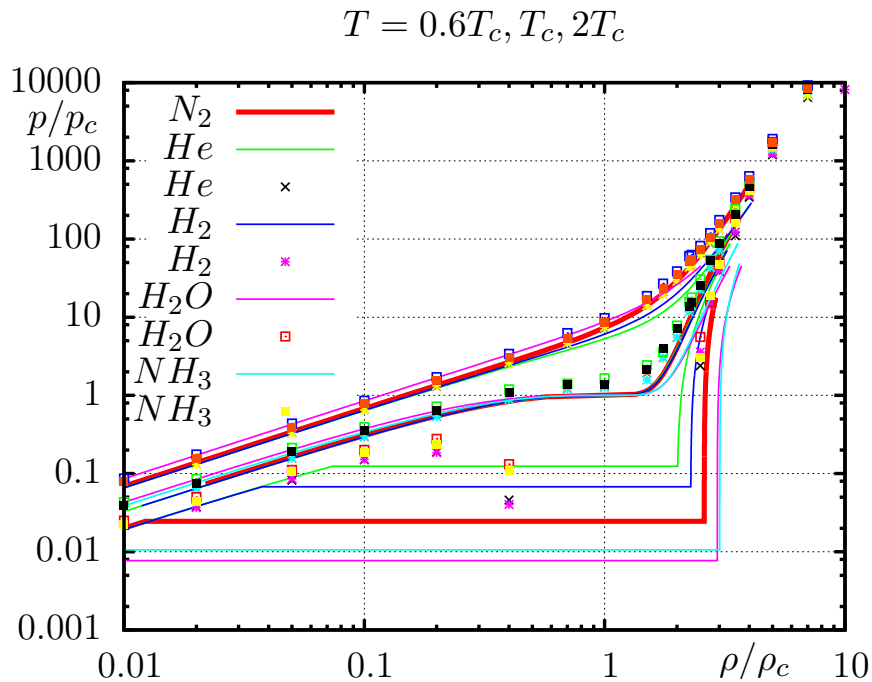
$$\gamma = \left(\frac{\partial p}{\partial \rho}\right)_S \frac{\rho}{p} = \left(\frac{\partial p}{\partial \rho}\right)_T \frac{c_p}{c_v}\frac{\rho}{p}.$$

Potential calibration. Critical point

$k_B T_c/\varepsilon = 1.326,\ \rho_c b^3/m = 0.316.$



"Good" material.

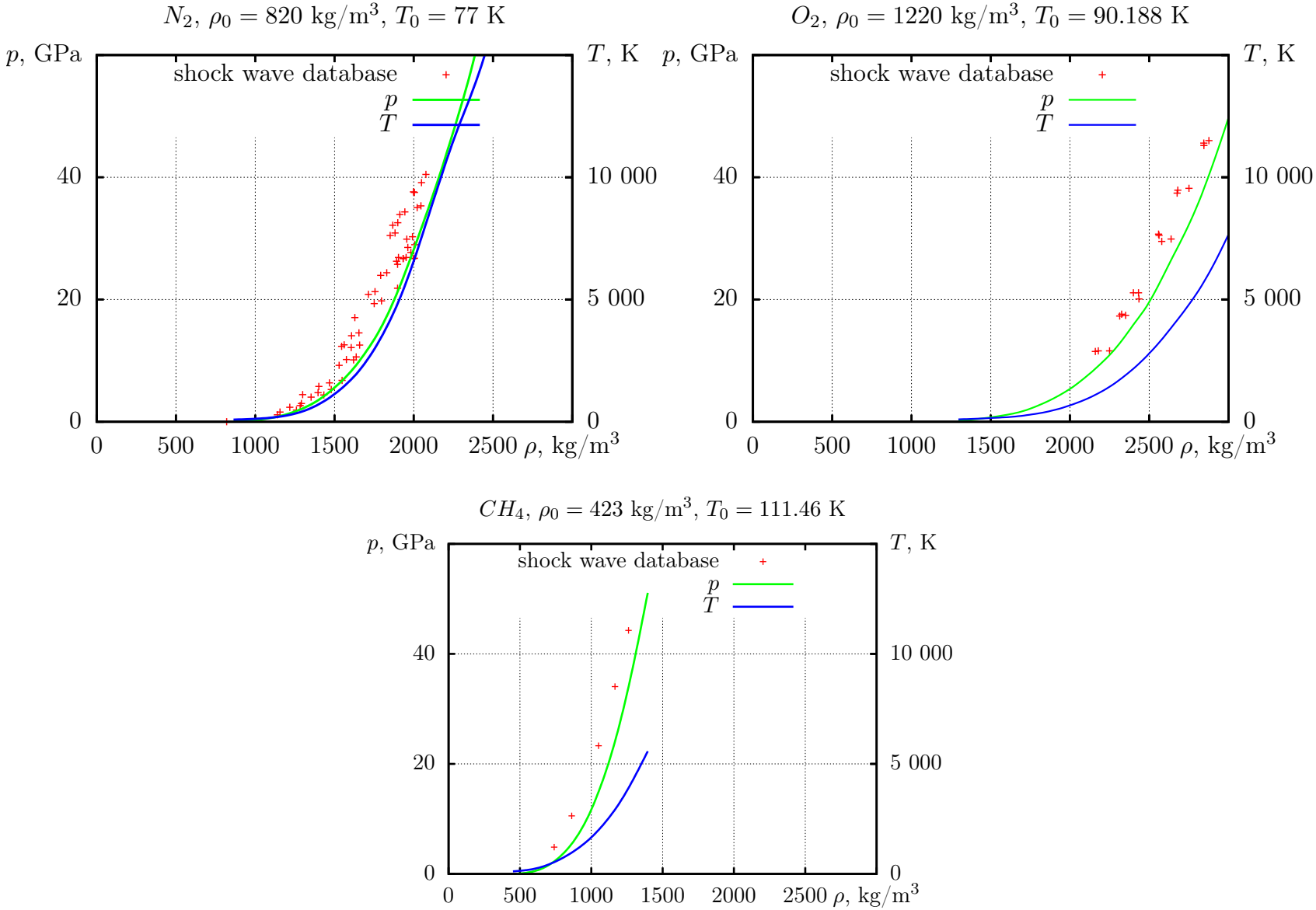


"Bad" material.

Problems: quantum effects for light gases, polar molecules, phase separation, no ionization.

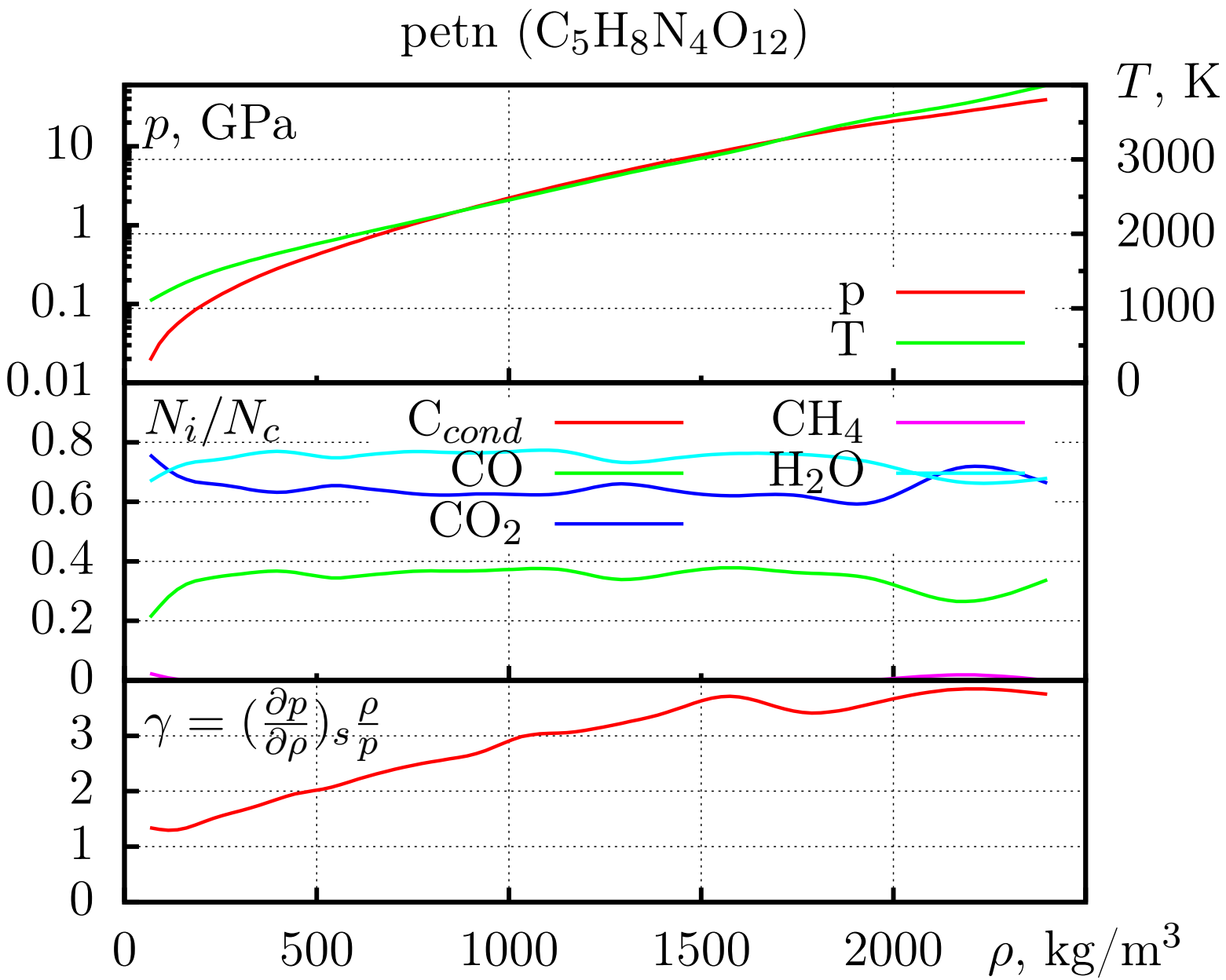
Calibration range: pressure from "0" to 1 GPa, temperature 100 - 10 000 K.

Potential calibration. Shock Waves

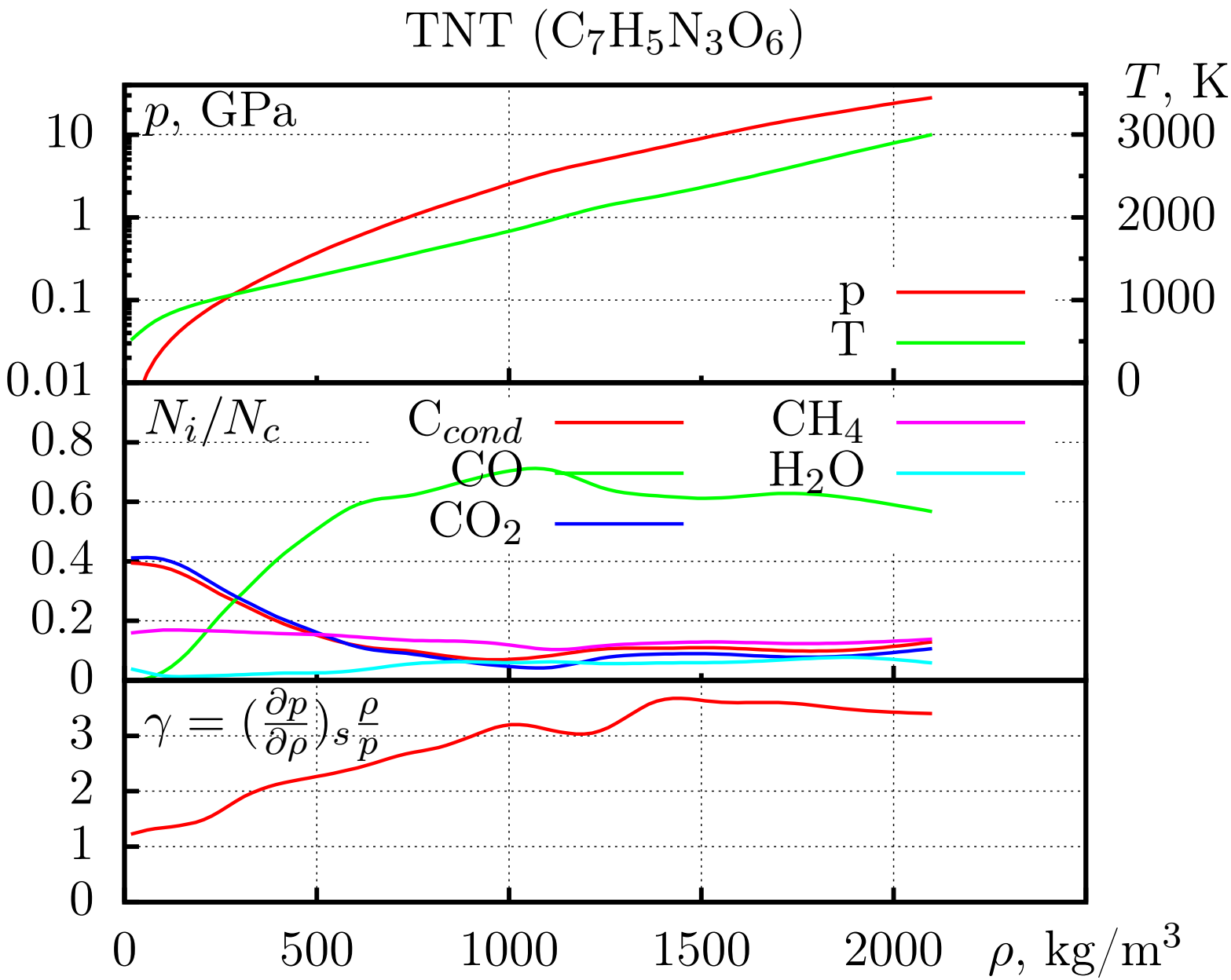


It is not possible to describe the entire range with a single set of potential parameters. For low pressures, Lennard-Jones, for high exp-6.

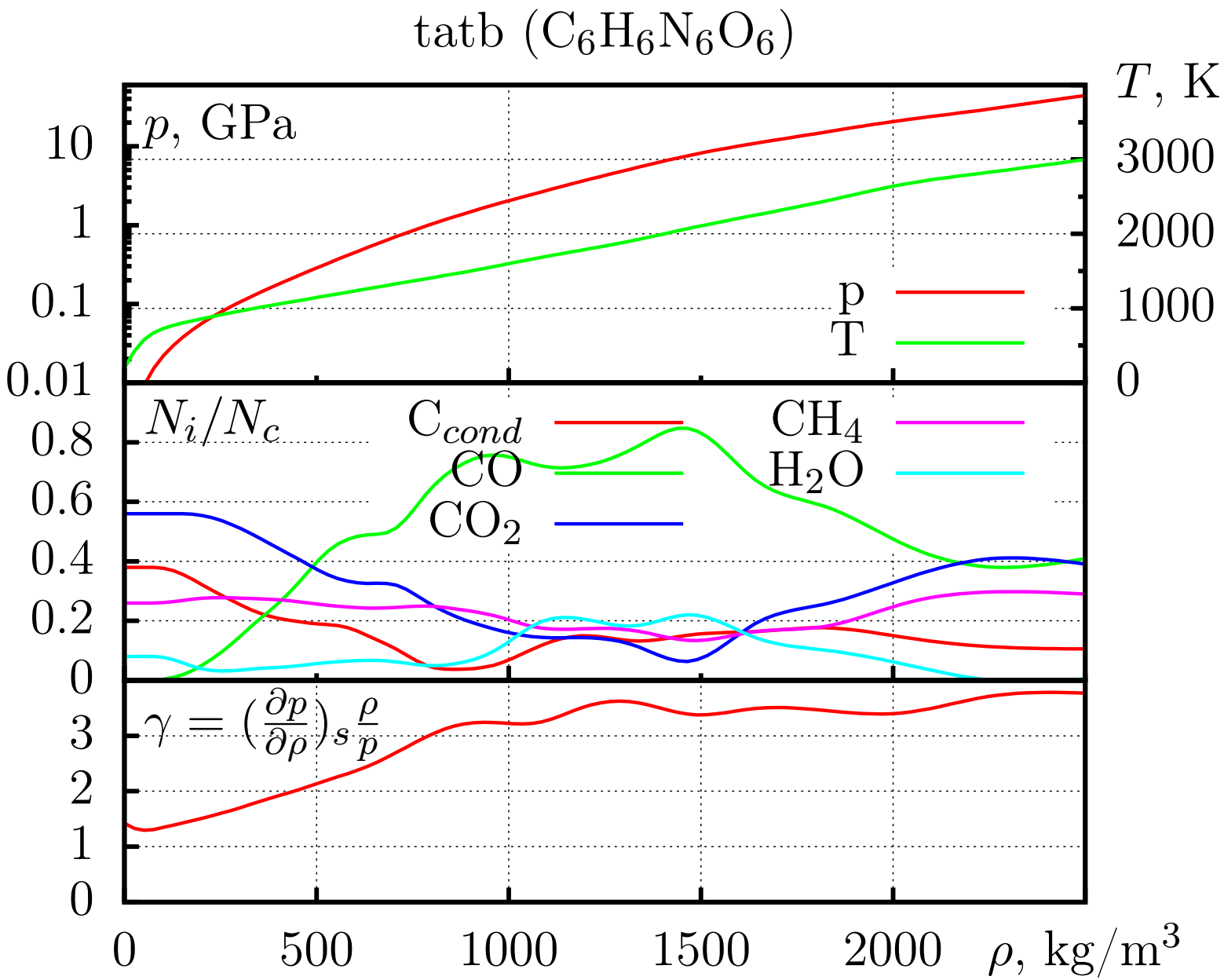
Adiabat unloading of detonation products (petn, $\rho_0 = 1770$ kg/m^3)



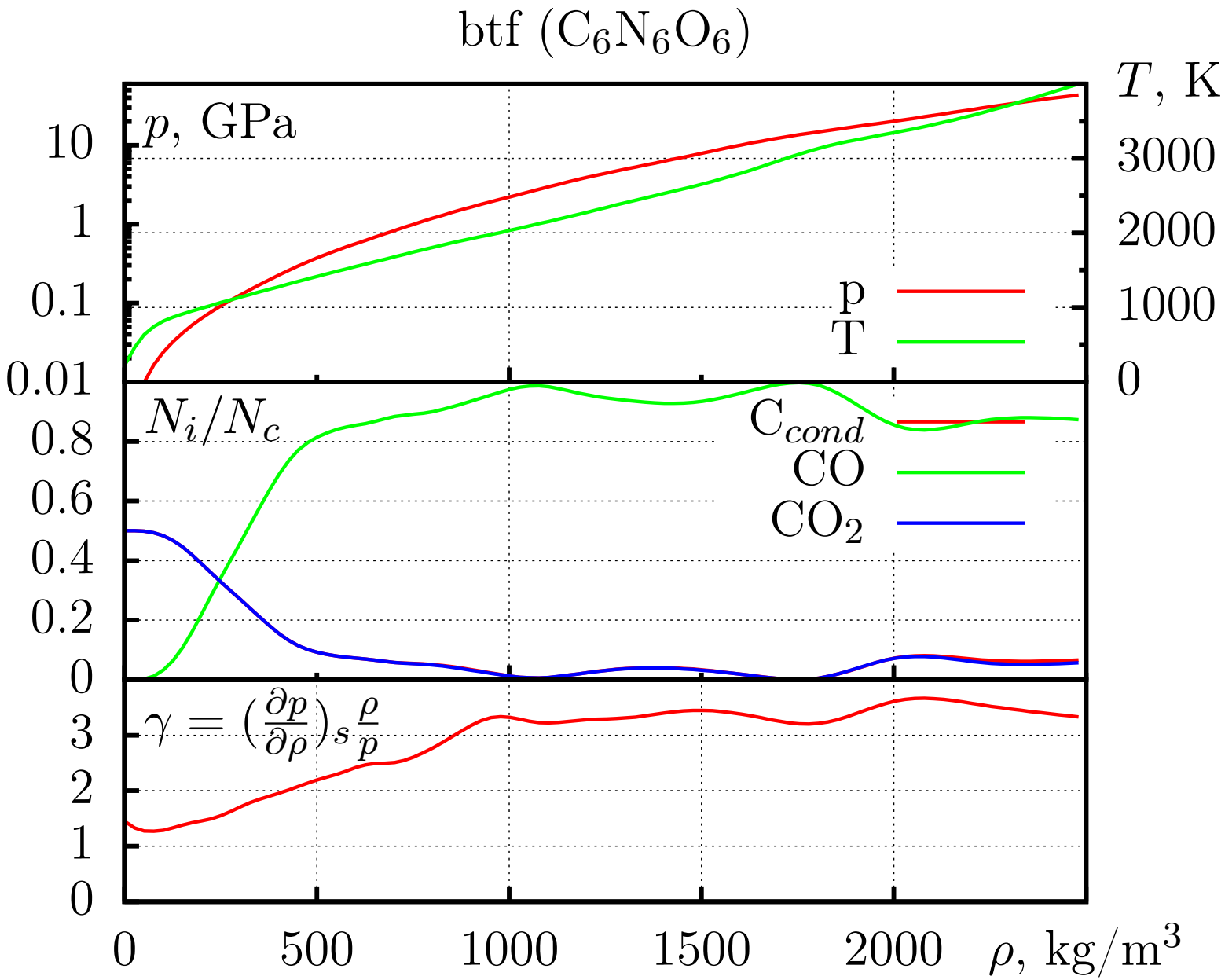
Adiabat unloading of detonation products (tnt, $\rho_0 = 1600$ kg/m^3)



Adiabat unloading of detonation products (tatb, $\rho_0 = 1860$ kg/m^3)



Adiabat unloading of detonation products (benzo three furoxane, $\rho_0 = 1860$ kg/m^3)



Conclusion

- A thermodynamic model of dense reacting gases was realized.
- Its testing (phase transitions, shock waves, adiabats of unloading detonation products) has been carried out.
- Achievements and issues identified.
- http://ancient.hydro.nsc.ru/chem.