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Abstract
Every condensed volatile or nonvolatile substance, including explosives, has an upper temperature boundary of their existence in the metastable state, i.e. the spinodal line. The spinodal line zone may be approach under intensive heating or another high-energy action. Near the spinodal every condensed reactive system transmutes into labile (unstable) state, i.e. it will be collapsed. The self-accelerate combustion and explosion processes we consider as result and development of thermodynamics stability loss which accrse near spinodal line. The spinodal zone may be approach with intensive heating during process of ignition, steady-stable combustion front propagation processes.

This communication summarized the many years experimental and theoretical study of upper metastable phase state boundary (spinodal) and the specific pre-spinodal effects which take place near this boundary. Present day theory of combustion and explosion has been elaborated for the gas phase only, which has neither spinodal nor spinodal collapse. Therefore, the “gas theory” does not take into consideration any pre-spinodal physical or chemical effects (spinodal limitations of any physical properties: density, conductivity, and heat capacity). Mathematical models of “Gas theory” are especially invalids in the vicinity of the spinodal line. The new concept suggested overcomes this drawback and provides correct and adequate to physical nature new mathematical models for condensed reactive systems transformation. New relationships are developed, particularly, for thermal conduction equation, heat release function, adiabatic ignition delay period of self-ignition etc. They allow to make more precise the calculations and describing of combustion and explosive processes of condensed reactive systems.
Extended Abstract

The temperature of reagents during the processes of combustion, ablation, laser material treating, explosion, etc. may be highly elevated and reach the upper temperature boundary of a metastable state, i.e. spinodal line. The position and spinodal parameters (p, v, T) are determined from the equation of state with the aid of the condition of inner thermodynamics stability: the second variation of Gibbs free energy is equal to zero for a given material [1]. The spinodal parameters may be determined if we know the equation of state by calculating the dp/dv and dT/dv derivatives and equality them to zero. However, the absence of reliable equations of state correctly describing the thermodynamic properties has long prevented us from determining spinodal parameters. The wide-range equation of state suggested recently in [2,3] make it possible to very accurately calculate the position the r of the spinodal. The spinodal parameters and its kinetic analogues - attainable superheating temperature T_l which insignificantly differs from spinodal line temperature at given pressure may be estimated experimentally. Suddenly, practically it is not possible to reach or approach the spinodal zone or attainable superheat temperature with the aid of traditional thermal analysis methods because of low heating rates. The earlier investigations have shown [4] that at an attainable superheat temperature in the vicinity of the spinodal line the process of the homogeneous nucleation intensifies very much, intermolecular action decreases, mechanism of the chemical reactions can change and the reactivity of products increases sharply. Near the temperature T_l the reaction rates are higher than ones predicted on the basis of the arrhenius monomial aquation. This processes make it difficult to fulfill the thermo-analitical experiments. Traditional methods and technique did not allow obtaining these data because the rates of sample heating are very low (from 2 to 50 K/min.)

High-accuracy results can be obtained by the “heat-probe”[4-6], and our contact thermal analysis [7-9] methods. The rates of a sample heating reach 10^5-10^7 K/s. in this methods. The experimental data for various substances are presented in this communication including kinetics parameters and values of T_l for energetic materials.
Many mathematical models in contemporary combustion theory comprise monotonic continuous function of temperature without respect to spinodal restrictions. The above mentioned spinodal boundary parameters should be taken into account in mathematical modeling of chemical and physical transformations occurring in the materials, because beyond the spinodal line the system, as such, no longer exists, because of the instability of vibrations of anharmonic oscillators responsible for retaining the initial state and composition of the material.

The mathematical corrections for spinodal restrictions are introduced in the following relationships which are presented in the communication:

1. The single-stage kinetic equation for thermolysis,
2. Adiabatic ignition delay (introduction period of self-ignition),
3. Various conditions of ignition of energetic materials.
4. Propagation velocity of the combustion front in condensed matters.
5. Heat release function,
6. Thermal conduction equation with heat release,
7. The overall reaction rate constant of thermolysis of condensed systems,
9. Ultimate velocity of linear pyrolysis of polymers,
10. Frequency of sample explosion at a given mechanical action (vibration, impact etc.),
11. Low and high limits of sensibility with impact loading,
12. Reaction rates under the influence of the axial vibrations,

The analysis performed has demonstrated that the upper temperature boundary of phase state can be take into account by introducing appropriate corrections in mathematical modeling of reactions and heat mass-transfer processes [7-13]. The comparisences of the traditional and developed description of combustion and explosive processes are presented in this communication.
References

1. Muenster, A. Chemische Thermodynamik (Chemical Thermodynamics), Berlin, Akademie Verlag, 1969.