CONCLUDING REMARKS

Investigations have revealed that occurrence of HPV distinguishes fundamentally CS burning from combustion of gaseous mixtures. Chemophase transformations parameters are to be included in the set of equations describing mathematical models of CS burning; therefore, these models are much more complicated than those of gaseous mixtures. Chemophase transformations intensity and rates of surface, and, particularly, of bulk, evaporation (coefficient f_{ev}) determine the feasibility and specify the conditions for occurrence of one or another CS burning regime, namely, flameless burning, mild thermal flare, flare with a bang, deflagration (its accleration), subdetonation, and its possible transition to detonation as well as mechanical activation and exitation of EM burning.

Appearance of new methods of thermal and chemical analysis, refinement of numerical techniques greatly facilitated development of the combustion theory of CS. Stages of CS thermolysis were investigated and flame structure of many EM was ascertained [58], kinetic parameters of individual reaction steps were assessed. The combustion models of condensed systems were developed. Nonetheless, there are many unsolved problems [59], in particular, inconsistency of the calculation results and experimental data. A considerable scatter of the kinetic characteristics of CS thermolysis determined by various techniques is one of the reasons of such a discrepancy. The experimental data on the activation energies for thermolysis of even such an EM as HMX range between 108 and 221 kJ/mol and the preexponential factor z varies from $3 \cdot 10^8$ to $6 \cdot 10^{19}$ s^{-1} [59]. This difference in the activation energy E and preexponential factor z values results in calculated ignition delay times ranging between 1 and 1000 s [69], and, consequently, in a great discrepancy between the parameters calculated by all the above-mentioned formulas in which activation energy E and preexponential factor z appear as parameters. There is no common opinion concerning the mechanism of thermal

decomposition reactions of many CS and EM which are the components of rocket propellants and of thermal protection coatings.

In analyzing the models of CS burning, one has to state that none of these models yield correct calculated burning velocity values for CS or isotherm spreading velocity in thermal shielding materials which would consistent with experimental data [60]. Feasibility of a quantitative assessment of the effect exerted by various factors on a CS burning process is a positive contribution to investigations.

The generalized notion of the limiting temperature to which CS can be preheated according to K. K. Andreev [1] was supported both experimentally and theoretically in many works mentioned in the present book. It should be noted that the limiting temperature was found for the first time for composite material binders in [61], its value was treated in [6,62]. Later on, other experimental data on attainable superheating temperature of polymers and other CS were reported [6, 22, 23, 25, 26, 28–31, 33]. However, achievements in this area have not always been taken into account in calculations of CS combustion processes. It is not difficult to demonstrate by examples that modeling of combustion processes without allowing for the boundary of a CS phase state can lead to unrealistic results.

It is established that as the rate of sodium azide heating increases from 2.5 to 10 degrees per minute, the heat-release peak shifts from 426 to 450 °C [64]. If dissociative phase transformation is disregarded in the calculations and calculations are performed solely with the use of kinetic relationships for chemical reactions, based on kinetic formulae (2.1)–(2.4), one can conclude that at a heating rate of 10^3 K/s, the heat release peak would shift to an unrealizably HT of 8000 °C. However, experiment [64] shows that in sodium azide burning, nitrogen evolution starts at 450 °C, while the combustion temperature (in a mixture with 10% $CoCl_2$) does not exceed 590 °C. Obviously, inclusion of the attainable superheating temperature of this compound (550 °C [6]) in kinetic calculations would allow more realistic results to be obtained in depicting burning of this compound and other primer explosives.

We present another example, namely, AP burning. At a heating rate of 10^3 K/s, which is inherent in AP burning, the burning surface temperature calculated without allowance for the attainable superheating temperature is 4–6 times higher than the real burning surface temperature of AP. The prediction contradicts the available experimental data (see Fig. 2.30). Allowance for phase transformations of a dissociative sub-

limation type alone makes it possible to more adequately simulate the observed pattern of burning of AP and primer explosives. Assessment of the nucleation frequency in mechanically impacted samples permitted the random character of ignition spot formation in hammer drop tests with a probability (frequency ratio) of flashes characterized by Poisson's distribution and normal probability distribution law to be accounted for [65]. An increase in the intensity of HMX surface heating by laser radiation from 35 to 60 W/cm^2 by increasing T_0 to 170 °C or introducing of additives did not raise T_s above T_ℓ. At the same time, calculations with allowance for HMX thermolysis kinetics only, e. g., by the Zel'dovich equation with no T_ℓ taken into account, predict unrealistic T_s temperature values tens and hundreds of degrees higher than T_ℓ.

Of fundamental importance for calculations of CS burning parameters is the experimentally established significant discrepancy in the mechanisms of mass reduction in the course of CS burning in LT and HT regions. At heating rates observed within the combustion front of solid rocket propellants and other CS and ranging from 10^4 to 10^6 K/s, the burning surface temperature is controlled mostly by CS dissociative boiling up or sublimation. In this case, combustion proceeds in the diffusion (in terms of heat) regime. The kinetic characteristics of chemical reactions proper affect the burning velocity in this regime only little and the burning surface temperature is stabilized at the attainable superheating temperature level. In this case, the CS burning velocity is proportional to the heat flux supplied to the burning surface. The basic combustion parameters calculated in the HT regime are the overall heat released in the course of CS gasification at the burning surface Q_Σ^s, temperature T_ℓ, and thermal and physical characteristics. The weak dependence of high-speed CS burning parameters on the kinetic thermolysis characteristics implies that uncertainty of their determination at LT affect only little the simulation results and that of the decisive importance is an accurate assessment of heats of transformations. Reliable scanning calorimetry techniques are developed to measure heats of transformations Q_Σ^s [66, 67].

Accounting for CPT allows one to bring together the results of calculations and experiments on EM combustion.

Classification of EM according to their sensitivity to impacts with no allowance for CPT and for a relation between combustion front propagation velocity and that of heat propagation does not seem properly grounded. This relation provides a simple answer to the question, why

such EM as TNT and HMX can burn in a slow burning regime whereas primary explosives never burn in this regime. The boiling regime with bubbling and decomposition never arises in them because of their high rigidity; therefore, the combustion front spreads at a velocity close to the HPV. Quantitative estimates of parameters f and f_t permit a criterion of safe handling of EM to be formulated:

$$T_m \leqslant [T]$$

where T_m is the maximum temperature at the most preheated CS spot and $[T] = T_\ell/n_{sf}$ where n_{sf} is the safety factor and $[T]$ is the admitted heating temperature.

Incorporation of temperature T_i (at which CS thermolysis starts) in the CS combustion model makes it possible to ascertain the condition for CS burning stability by lowering the combustion temperature in the gas phase or from a pressure drop and for SHS process stability.

The use of a hyperbolic wave heat conduction equation is a promising approach in the theory of CS combustion to calculating propagation velocities and other parameters of the combustion front in primary EM and to distinguishing them as a specific group, thermal, physical, and physicochemical properties of which differ from those of HE.

The mechanical activation (i. e., nonthermal) nature of EM flash caused by an impact is supported by observation of a thermolysis reaction in thermodynamically unstable fluoroplast [4] in hammer drop tests of thin Teflon–aluminum layers [39].

The limited size of the present book precludes detailed description of combustion processes in the gas phase behind the CS burning surface. We confine ourselves only to references in this area published recently [58,68].

Information about practical application of high-rate heating to processing of raw materials, including petroleum products, in chemical technology can be found in [69–72].