TEMPERATURE DEPENDENCE OF RATE CONSTANTS
AND NUMERICAL METHODS FOR KINETICS
PROBLEMS

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1. Kinetics problem. Kinetics of reactions is described by a system of ODEs. In case of dual reactions it can be written as follows:

\[ \frac{dn_j}{dt} = \sum (\pm) K_{ij} n_i n_j, \quad 1 \leq i, j \leq J. \]  

Here \( n_j \) are concentrations, \( T \) is temperature, “+” is used for reactions with production of component number \( j \) and “−” is for reactions with its consumption; \( K(T) \) is rate constant.

There are 2 main difficulties: 1) to find reliable dependencies \( K(T) \) because the laws of interaction between colliding particles are usually not known; 2) to solve the system (1) numerically, for the rate constants can vary within several orders of magnitude so the system is superstiff.

2. Rate constants. Chemists use traditional approximations \( K(T) = AT^k \exp\left(\frac{-E}{T}\right) \). Values of \( A, K, E \) given in reference books do not stand any physical critics. We have conducted quantum mechanical derivation of rate constants in the case of neutral gas molecules and obtained

\[ K_d(T) = C \sqrt{\frac{\pi}{4} E + T}, \quad K_r(T) = C \sqrt{\frac{m_{b1} m_{b2}}{m_{a1} m_{a2}}} \sqrt{\frac{\pi}{4} E + T} \exp\left(\frac{-E}{T}\right) \]

for direct (non-threshold) and reverse (threshold) reactions respectively.

Here \( E \) is the reverse reaction threshold, \( m \) are particles’ masses and coefficient \( C \) depends on the intermolecular interaction law only.

3. Hydrogen combustion. We have considered hydrogen combustion in oxygen as an example and accounted for components \( O, H, H_2, O_2, OH, H_2O, HO_2, H_2O_2, O_3, O_4 \) involved in 24 direct and 24 reverse reactions. These data were processed to the form (2). The resulting tables can be recommended as the most reliable reference data for \( T < 10^4 \) K.

4. Numerical method. Classical explicit schemes are completely inapplicable for system (1) and implicit schemes are too labor-consuming.

A special chemical scheme was proposed in [1], though its accuracy \( O(\tau) \) was not high. Now we have constructed a scheme with better accuracy \( O(\tau^2) \) and higher robustness.