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Comparison Between RCCE and Shock Tube Ignition Delay Times at Low Temperatures

The rate-controlled constrained-equilibrium (RCCE) method is a reduction technique based on local maximization of entropy or minimization of a relevant free energy at any time during the nonequilibrium evolution of the system subject to a set of kinetic constraints. In this paper, RCCE has been used to predict ignition delay times of low temperatures methane/air mixtures in shock tube. A new thermodynamic model along with RCCE kinetics has been developed to model thermodynamic states of the mixture in the shock tube. Results are in excellent agreement with experimental measurements.

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1 Introduction

The development of predictive tools for combustion kinetics involves the identification of important chemical species and reaction pathways as well as the compilation of relevant thermochemical data and rate constant parameters. Ideally, the most accurate approach to this problem is to include all possible species and reactions of any importance to predict, within the specified uncertainty, a wide variety of experimental data. Such models are frequently referred to as detailed kinetic models (DKM). Modelers face a huge challenge because of the complexity of these models since it can include hundreds of species and thousands of elementary reactions for even relatively simple fuels. Moreover, a small change in the rate constants of these reactions can result in very different system behavior, such as burning speed and fuel consumption rate. Therefore, accurate prediction of the rate constants is critical for the development of a complex kinetic mechanism. However, the rate data could be quite uncertain especially for reactions involving heavy molecules, and involve guess work based on structural similarities.

Furthermore, when the DKM method is coupled with transport equations, the computational tasks often become formidable due to the intrinsic presence of a wide range of time and length scales, which may result in the well-known stiffness difficulties. Such difficulties have motivated the development of reduction techniques during the past three decades. Many methods have been proposed to reduce the complexity of the model while maintaining the degree of detail of predictions as described by authors [1]. In this article, the RCCE has been used to determine ignition delay of methane/air mixtures at low temperatures.

RCCE method was first introduced by Keck and Gillespie [2,3], and was improved by Metghalchi and coworkers [4–10]. It is based on the second law of thermodynamics. It assumes that slow reactions in a complex reacting system impose constraints on its composition which retard its relaxation to complete equilibrium. Fast reactions equilibrate the system subject to the constraints imposed by the slow reactions. As a consequence, the system relaxes to complete chemical equilibrium through a sequence of constrained-equilibrium states at a rate controlled by the slowly changing constraints. In RCCE, consistent with classical thermodynamics, the number of constraints needed to describe the dynamic state of the system within experimental accuracy can be very much smaller than the number of species in the system. Therefore, fewer equations are needed to describe the system's

evolution. This will result in savings in computation time, which is the main purpose of any modeling or reduction technique. Given the fact that in the entire body of thousands of chemical reactions perhaps less than hundred have rate constants known better than a factor of two, this feature of RCCE could help remove a great deal of uncertainty from the system by properly invoking the constrained-equilibrium assumption. Reactions which do not change any constraint are in constrained-equilibrium and need not be specified. Nonetheless, a successful implementation of the RCCE method depends critically on the choice of constraints and knowledge of the rates of the constraints-changing reactions is required. RCCE was further developed to predict ignition delay of methane/air mixtures at high temperatures [1]. The results were in excellent agreement with experimental measurement. Since the ignition delay at high temperature are very low, constant volume and constant energy thermodynamic model was used. But, for temperature ignition delay, this model does not work.

The purpose of this paper is to develop a new thermodynamic model along with using RCCE kinetics for predicting ignition delay of methane/air mixtures at low temperature in shock tube.

2 Mathematical Modeling Using RCCE Method

The changes in the species composition of a system are the result of chemical reactions of the form

$$\sum_{j=1}^{N_s} \nu_{jk}^+ A_j \rightleftharpoons \sum_{j=1}^{N_s} \nu_{jk}^- A_j, \quad k = 1, \dots, N_r \quad (1)$$

where A_j is the symbol of species j , N_r is the number of reactions, N_s is the number of species, ν_{jk}^+ and ν_{jk}^- are the forward and reverse stoichiometric coefficients of species j for reaction k . For a given mechanism, the rate equation for each species j is given by

$$\frac{dN_j}{dt} = V \sum_{k=1}^{N_r} \nu_{jk} r_k, \quad j = 1, \dots, N_s \quad (2)$$

where $\nu_{jk} = \nu_{jk}^- - \nu_{jk}^+$ is the net stoichiometric coefficient of species j in reaction k . Also, r_k^+ , r_k^- and $r_k = r_k^+ - r_k^-$ are, respectively, the forward, the reverse, and the net rates of reaction k and N_r is the number of reactions. The energy equation for an adiabatic, closed homogeneous system can be written as

$$\frac{dE}{dt} = -p \frac{dV}{dt} \quad (3)$$

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where E is the energy of the mixture, p is the pressure, and V is the volume of the reactor. Assuming an ideal gas mixture, the energy of the system can be expressed as

$$E = \sum_{j=1}^{N_s} N_j e_j(T) \quad (4)$$

where $e_j(T)$ is the specific internal energy of species j , and the equation of state becomes

$$pV = \sum_{j=1}^{N_{sp}} N_j RT \quad (5)$$

Equations (3)–(6) form a set of $N_s + 2$ equations for $N_s + 2$ unknowns (T, p, N_j).

2.1 Rate Equations for the Constraints. The constraints are assumed to be a linear combination of species composition present in the system. They can be written in the form

$$C_i = \sum_{j=1}^{N_{sp}} a_{ij} N_j \quad i = 1, \dots, N_c, \quad (6)$$

where a_{ij} is the value of the constraint i for the species j and N_c is the number of constraints. The constrained-equilibrium composition found by minimizing the Gibbs free energy subject to a set of constraints using the method of Lagrange multipliers is

$$N_j = Q_j(T, V) \exp\left(-\sum_{i=1}^{N_c} a_{ij} \gamma_i\right) \quad (7)$$

where

$$Q_j(T, V) = \frac{P_0 V}{R_u T} \exp\left(-\frac{\mu_j^0(T)}{R_u T}\right)$$

is the partition function of species j . $\mu_j^0 = (h_j^0 - T s_j^0)$, and γ_i are, respectively, the standard Gibbs free energy of species j , and the constraint potential (Lagrange multiplier) conjugate to the constraint i . It is important to notice that once the value of constraint potentials are obtained, the mole number of all species can be obtained through Eq. (7).

The detailed derivation of RCCE equations in constrained potential form can be found in earlier works [7]. The equations governing the constraint potentials can be obtained as

$$\sum_{n=1}^{N_c} C_{in} \frac{d\gamma_n}{dt} - C_{iV} \left(\frac{1}{V} \frac{dV}{dt}\right) - C_{iT} \left(\frac{1}{T} \frac{dT}{dt}\right) + \sum_{k=1}^{N_c} b_{ik} r_k = 0 \quad (8)$$

where

$$C_{in} = \sum_{j=1}^{N_s} a_{ij} a_{nj} [N_j],$$

$$C_{iV} = \sum_{j=1}^{N_s} a_{ij} [N_j],$$

$$C_{iT} = \sum_{j=1}^{N_s} a_{ij} \frac{E_j}{RT} [N_j],$$

$$b_{ik} = \sum_{j=1}^{N_s} a_{ij} (\nu_{jk}^+ - \nu_{jk}^-)$$

To close the system of equations, Eq. (8) is coupled with the energy equation that takes the following forms:

$$\sum_{n=1}^{N_c} C_{en} \frac{d\gamma_n}{dt} + C_{eV} \left(\frac{1}{V} \frac{dV}{dt}\right) + C_{eT} \left(\frac{1}{T} \frac{dT}{dt}\right) - \frac{dE}{dt} = 0 \quad (9)$$

where

$$C_{en} = -\sum_{j=1}^{N_s} a_{nj} E_j [N_j]$$

$$C_{eV} = \sum_{j=1}^{N_s} E_j [N_j]$$

$$C_{eT} = \sum_{j=1}^{N_s} \left(C_{vj} T + \frac{E_j^2}{R_u T} \right) [N_j]$$

$$\frac{dE}{dt} = -\frac{p}{V} \frac{dV}{dt}$$

C_{vj} is the frozen molar heat capacity of species j at constant volume and p is pressure. Once the differential equations for the γ vector are solved, the constrained-equilibrium composition of the system can be found at each time step from Eq. (7). The procedure to obtain the initial condition for the constraint potentials has been discussed in detail in Ref. [4].

3 Modeling Combustion Process in Shock Tube

3.1 Nonvalidity of Constant Energy Constant Volume (E, V) Assumption in Shock Tubes at Low Temperatures. Recent studies by Chaos and Dryer [11] have demonstrated that the assumption of constant volume constant energy in shock tube is invalid at low temperatures. Shock-induced self-ignition of undiluted fuel/air mixtures at the conditions of interest are characterized by relatively long ignition delay times on the order of a few milliseconds. The ignition event is accompanied by marked changes in pressure and energy release. Hence, ignition under these conditions is strongly coupled to the thermodynamic state and fluid dynamics of the gas behind the reflected shock wave. One-dimensional analyses predict that the gas behind a reflected shock should be stationary and have uniform thermodynamic properties over the entire test volume. Pre-ignition chemistry might occur in the case of hydrocarbons/air mixtures as a result of negative temperature coefficient behavior (i.e., two-stage ignition). However, even for dilute mixtures, unavoidable nonidealities exist in the shocked gases, due to the presence of boundary layers. Incident shock attenuation, boundary layer growth, and shock-wave/boundary-layer interactions lead to nonuniform pressures and temperatures behind the reflected shock, which gradually increase with time.

Furthermore, residual gas velocities may exist behind the reflected shock wave that also contribute to pressure gradients along the shock tube axis [12,13]. These nonidealities can be minimized by using large diameter shock tubes, dilute fuel/oxidizer mixtures, and short test times (less than about 500 μ s) [14,15]. The latter two options typically are not applicable to ignition studies of undiluted fuel/air mixtures. For highly reactive mixtures, the above-mentioned phenomena are further compounded by the fact that at high pressures and lower temperatures, ignition is inhomogeneous with “local hot spots” leading to a homogeneous transition to detonation [16–19]. Gas expansion due to the finite exothermicity of the initial reaction sites coupled with the high-speed of sound in the shocked region can induce further increases in pressure throughout the gases behind the reflected shock, prior to the main ignition event.

Dryer and Chaos found that changes in the thermodynamic state of the gas behind the reflected shock wave are likely to be

significant (especially for longer observation times and higher energy density fuel/oxidizer mixtures) and, thus, can have a pronounced effect on kinetic observations and the ignition process [20,21]. In some of their experiments [22–26], they found that pressure increases by a factor of 2 prior to ignition can be observed for the case of toluene. In such instances, kinetic modeling of ignition delay should no longer be performed under the common assumption that the shock tube behaves as a constant volume system with constant internal energy. The pressure history in these cases is needed; however, this information is infrequently provided along with reported shock tube ignition delay measurements.

Even with this information in hand, the general modeling approach for analyzing shock tube data has typically been to apply constant U, V zero-dimensional modeling predictions to interpret the reported data. An interesting example is provided by the study of Davidson et al. [25] who acknowledged the presence of the pre-ignition pressure rise and noted that existing kinetic models failed to predict this pre-ignition activity. In their research, Davidson et al. mentioned that this behavior is caused by a chemical-kinetic process not predicted by the chemical-kinetic models used. The issues outlined above have received considerable attention recently, and pressure variations prior to ignition are identified and taken into account when interpreting and modeling shock tube data at low temperatures.

3.2 Introducing the Prescribed Pressure (H, P) Reactor.

Many techniques were implemented to solve this issue of pre-ignition pressure rise. In the case of shock wave-boundary layer interactions or ignition outside of the measurement volume, the postshock temperature profile in shock tube ignition time experiments is effectively higher than the post temperature profile expected in a true constant-volume experiment. In this case, experimental data underestimates the ignition delay time that would be expected in a true constant-volume experiment due to the temperature increasing nonidealities that are present in a shock tube [27]. Therefore, a possible correction for the ignition delay time data is to estimate a temperature higher than the postreflected shock temperature that more accurately represents the “effective” temperature that drives chemical processes.

One more sophisticated approach is the one by Li et al. [28]. They proposed a kinetic tool, CHEMSHOCK, which treats time varying pressures coupled with chemical kinetics. CHEMSHOCK solves the coupled energy and chemical species system of differential equations using a two-step process: at every time step the system is first solved assuming constant (E, V) conditions, and then pressure and temperature are adjusted isentropically to match the measured pressure profile while keeping the chemical composition fixed.

Another method is to use a prescribed pressure (H, P) reactor model. So the pressure profile traces $P(t)$ measured will be used as input to solve for volume and temperature, instead of solving for pressure and temperature like in the prescribed volume (E, V) reactor. Even though pressure profiles were not reported for modeling purposes, we have approximated the traces as having constant pressure for a finite amount of time, τ , and then increasing linearly with a slope α until the moment of ignition as shown in Fig. 1. The mentioned parameters, τ and α , are dependent on fuel, initial temperature, pressure, and equivalence ratio. Therefore, these parameters need to be determined experimentally. Due to lack of the experimental data of pressure as a function of time, parametric study has been done to determine the best pair of parameters τ and α .

4 Comparison in Ignition Delay Time Between RCCE and Experiments

Figure 2 shows comparison in ignition delay times between shock tube experiments of Huang et al. [29] and both types of

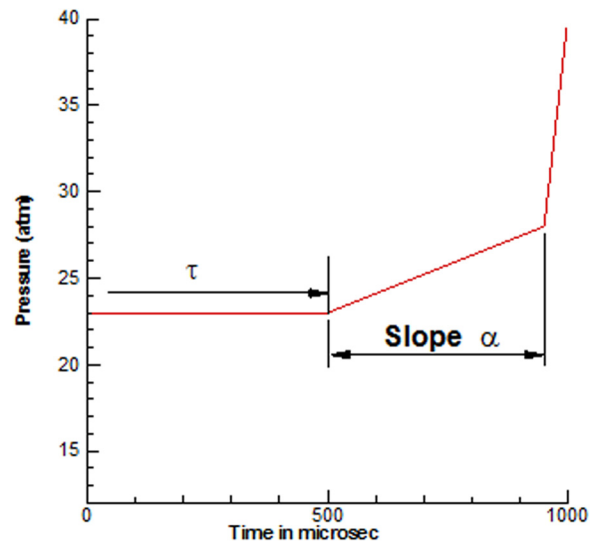


Fig. 1 A typical prescribed pressure profile for CH_4/air mixture in shock tube

reactors: prescribed volume and energy (E, V) reactor and the prescribed pressure and enthalpy (H, P) reactor. Ignition delay time was defined as the time when temperature reaches 400 K over the initial temperature. The comparison was made at $\Phi = 1.0$, $P = 23$ atm and temperature ranging from 1076 to 1309 K. Labeled in red are experimental data, while the green and blue symbols represent the (E, V) and (H, P) reactors, respectively. Clearly the effect of the prescribed pressure is more apparent at low temperatures. The constant volume constant energy approach is valid for temperatures higher than 1150 K, but for lower than that, predictions don't fall within experimental accuracy. A parametric study was done to determine the values of τ and α . τ was varied from 0.5 to 1.2 ms, and α from 1 to 6%/ms. A set of $\tau = 0.7$ ms and $\alpha = 4\%/ms$, yielded good results and improved the accuracy of RCCE predictions. These values of τ and α agree well with the values provided by Davidson's (private communication). Note that for temperatures higher than 1150 K, the predictions using the prescribed volume (E, V) reactor match those calculated using a prescribed pressure (H, P) reactor. This indicates that the assumption of constant volume constant energy is valid for

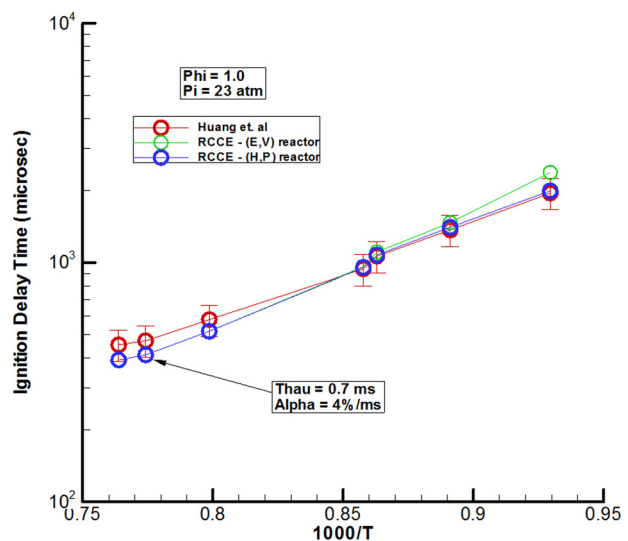


Fig. 2 Comparison of ignition delay times between RCCE and shock tube experiments [29] with a prescribed pressure profile with $\tau = 0.7$ ms and $\alpha = 4\%/ms$. Initial conditions are: $\Phi = 1.0$ and $P = 23$ atm and temperature varying from 1076 to 1309 K.

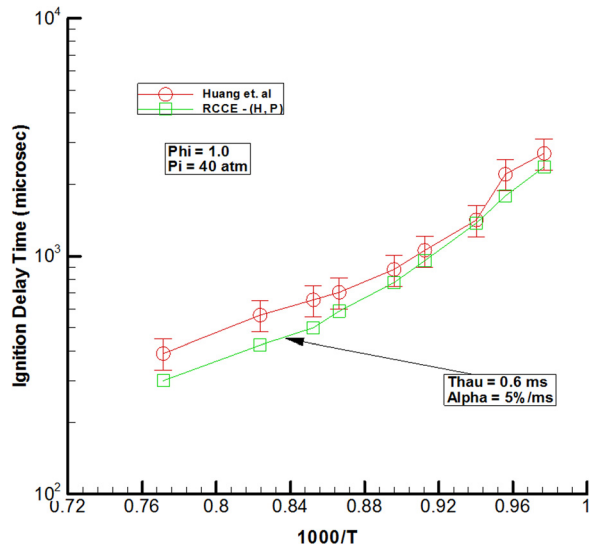


Fig. 3 C_1 chemistry-comparison in ignition delay time between RCCE and shock tube experiments [29] with a prescribed pressure profile with $\tau = 0.6$ ms and $\alpha = 5\%/ms$. Initial conditions are $\Phi = 1.0$, $P = 40$ atm, and temperature varying from 1085 to 1290 K.

temperatures higher than 1150 K, for a stoichiometric mixture at an initial pressure of 23 atm.

Figure 3 represents another comparison in ignition delay time with shock tube data from Huang et al. [29]. Ignition delays were measured at $\Phi = 1.0$, $P = 40$ atm and temperature varying from 1023 to 1296 K. A prescribed pressure profile was used as well with $\tau = 0.6$ ms and $\alpha = 5\%/ms$. Predictions fall within the accuracy of experiments, and the overall agreement between RCCE and experimental values is acceptable. Note that for temperatures higher than 1200 K, the model under-predicts ignition delay times at high pressures, but the overall agreement is acceptable.

5 Conclusion

A brief discussion is presented to explain and clarify the nonvalidity of the constant energy constant volume assumption for shock tube data at low temperatures. Moreover, possible solutions that can correct the experimental data have been presented, and the adjusted pressure profile technique was selected. At the end, a case study has been presented: Ignition delay times for CH_4 /Air mixtures from shock tube at low temperatures were used to validate RCCE. The predicted results of RCCE combined with prescribed pressure and enthalpy are in excellent agreement with experimental shock tube data.

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