

Research Article

Charged Species Concentration in Combusting Mixtures Using Equilibrium Chemistry

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Ionization in flames is of interest in the design and development of modern combustion devices. The identity and concentration of various charged species in reacting mixtures can play an important role in the diagnostics and control of such devices. Simplified chemistry computations that provide good estimates of ionic species in complex flow-fields can be used to model turbulent reacting flows in various combustion devices, greatly reducing the required computational resources for design and development studies. A critical assessment of the use of the equilibrium chemistry method to compute charged species concentration in combusting mixtures under various temperatures, pressures, and thermal disequilibrium conditions is presented. The use of equilibrium chemistry to compute charged species concentrations in propane-air mixtures performed by Calcote and King has been extended. A more accurate computational methodology that includes the effect of negative ions, chemi-ions (H_3O^+ and CHO^+), and thermal nonequilibrium was investigated to evaluate the suitability of equilibrium computations for estimating charged species concentrations in reacting mixtures. The results show that equilibrium computations which include the effects of H_3O^+ and elevated electron temperatures can indeed explain the levels of ion concentrations observed in laboratory flame experiments under lean and near-stoichiometric conditions. Furthermore, under engine-like conditions at higher temperatures and pressures, equilibrium computations can be used to obtain useful estimates of charged species concentrations in modern combustion devices.

1. Introduction

Ionization in flames has been a topic of research since the late 1940s [1–10]. Early investigations in this area were motivated primarily by defense applications such as the need to define the size and extent of radar targets, predict electromagnetic wave attenuation in propulsion and re-entry systems, and understand various communication-related problems. Another important application of ionized gas flows was in the area of power generation. Magnetohydrodynamic (MHD) power generation received considerable attention in the 1960s. MHD generators produce electricity directly from a fast moving stream of ionized gases without the need for any moving mechanical parts such as turbines and rotary generators. One of the main technical challenges in operating MHD generators is the creation and sustenance of the ions in the working fluid. Candidate working fluids included flow streams derived from combustion, noble gases such as argon and gas streams seeded with alkali metal vapors such as

Potassium and Cesium. The design and development of these MHD generators required the accurate computation of the charged species concentrations to determine the conductivity of the working fluid.) In recent years, research on ionization in flames has been spurred by the need for advanced ignition methods for engineering applications. Ultra-lean combustion in internal combustion engines and high-speed flows in aerospace applications (ramjets and scramjets) are two notable examples [1, 2]. Internal combustion engines represent applications characterized by low temperatures and high pressures ($T \sim 600\text{--}700\text{ K}$, $P \sim 15\text{--}40\text{ atm}$ at ignition) and low speeds (gas velocity $10\text{--}50\text{ m/s}$), whereas aerospace applications represent a case of moderate temperature, low pressure ($P \sim 0.1\text{--}1\text{ atm}$) and high velocity ($V \sim 500\text{ m/s}$). Given the emphasis on reduction of emissions in the power generation and transportation sectors, the role of ions in soot formation is another important area of study. Soot formation is believed to be influenced by charged species in fuel-rich hydrocarbon-air combustion. The main precursor

for soot formation is assumed to be the chemi-ion, $C_3H_3^+$, which is the dominant ion in fuel-rich hydrocarbon flames. Understanding the process of initiation and development of the combustion kernel plays a key role in design, development, and optimization of engineering applications using advanced ignition methods. Active radicals and charged species (electrons and ions) are believed to be important in the early flame development phase. Determining the identity and concentration of important species using both, experimental and numerical techniques, has been a topic of research since the late nineteen forties [5–11]. More recent studies on the topic can be found in [12–19]. Charged species concentrations in reacting mixtures can be evaluated using equilibrium chemistry or finite-rate chemistry (FRC) assumptions. Most of the numerical studies aimed at evaluating charged species concentrations in flames use finite-rate chemistry (see [12–16] and references therein) in low-pressure, laboratory flames using simple hydrocarbons such as methane. In power generating combustion devices such as internal combustion engines and gas turbines, combustion takes place under high pressure conditions with complex fuels and hence the mechanisms used to study combustion of simple hydrocarbons at low pressures would likely have to be extended considerably to produce reliable and accurate results.

In some of the earliest studies by Calcote and his co-workers, the concentration of positive ions in the combustion zone of a laboratory hydrocarbon flame ($P = 1 \text{ atm}$) was estimated to be about 10^{12} ions/cc using a simplistic mechanical model [5, 6] (although later experiments have shown the ion concentrations to be in the range of 10^9 – 10^{10} ions/cc [7, 11].) Calcote and King [10] sought to explain the positive ion concentration deduced from experimental measurements of current in stoichiometric propane-air flames by using equilibrium assumptions. They assumed that the combustion mixture consisted of a set of neutral species and an adiabatic flame temperature of 2200 K for a near-stoichiometric propane-air mixture at a pressure of 1 atmosphere. They computed the ion concentration under thermal equilibrium assumptions using the Saha equation (this technique will henceforth be referred to as the Calcote method). The following neutral species were considered in their computations: H_2 , N_2 , CO , CO_2 , H , OH , O , H_2O , O_2 , NO , Na , and C . Only reactions of the kind $M = M^+ + e^-$ were considered. Furthermore, a given ion concentration was computed assuming that only a single ionic species was present in the combustion mixture. For instance, to compute the concentration of H^+ ions, they assumed that the combustion products contained only H_2 , N_2 , CO , CO_2 , H , OH , O , H_2O , O_2 , NO , Na , C , H^+ , and e^- . Calcote and King reported that at 2200 K, NO^+ has the highest ion concentration at $1.7 \times 10^7 \text{ ions/cc}$ (excluding Na^+ and C^+), as shown in Table 1 of [10]. The concentration of the dominant ionic species, NO^+ , is well below the value of 10^{12} ions/cc estimated from experiments on stoichiometric propane-air flames. Given the large discrepancy between ion concentrations estimated from experimental data and equilibrium calculations, Calcote and King concluded that “ions are produced not by thermal processes but by chemi-ionization or events similar to those

using abnormal electronic excitation in flames. The results have also been taken as evidence that thermal equilibrium does not exist between the species in the flame front” [10].

The large discrepancy between the maximum ion concentration reported by Calcote’s computations and the estimates inferred from experimental data could stem from the restrictive assumptions and computational methodology used in Calcote’s calculations. Specifically, Calcote and King considered only positive ions and electrons in their equilibrium calculations (produced by thermal ionization). The presence of negative ions such as OH^- , O^- or O_2^- and positive ions such as H_3O^+ were ignored. While Calcote and King did conclude that thermal equilibrium does not exist between the ions and their parent species, and that chemi-ions could be responsible for the higher ion concentrations deduced from experiments, they did not extend their computations to include these effects. Goodings et al. [11] showed that one of the dominant charged species in rich CH_4 - O_2 flames is H_3O^+ and that its measured value is identical to the expected equilibrium value. Goodings et al. also showed that the measured concentration of H_3O^+ is $\sim 1.4 \times 10^{10} \text{ ions/cc}$, which is two orders of magnitude less than the $\sim 10^{12} \text{ ions/cc}$ estimated by Calcote. Additionally, Goodings et al. showed that the concentration of the second most dominant species, CHO^+ , is about three orders of magnitude less than that of H_3O^+ (see Table 1 in [11]). The importance of H_3O^+ in hydrocarbon-air flames is well known and has been reported in more recent studies using finite-rate chemical kinetic calculations. Similarly, recent studies have shown that the ion current in a constant volume chamber and HCCI engines can be explained well by using equilibrium assumptions and that H_3O^+ is indeed the dominant positive ion [17, 18].

While there are a considerably large number of studies using finite-rate chemistry to investigate charged species concentrations in laboratory and low-pressure flames, there is relatively little work done on the use of equilibrium chemistry methods to evaluate charged species composition in reacting mixtures. In this work, a more in-depth study of the equilibrium concentration in stoichiometric hydrocarbon flames is conducted by including the effects of chemi-ions and elevated electron temperatures, thus complementing Calcote’s initial work. Revisiting Calcote’s calculations to determine the appropriateness of using equilibrium assumptions for computing charged species concentrations in reacting mixtures can also benefit the development of fast and robust design/optimization tools for modern applications of plasma-based combustion systems which typically operate in the lean/stoichiometric regime (equivalence ratio < 1). Use of equilibrium chemistry computations for determining the concentration of combustion products is advantageous to using finite-rate chemistry calculations. Finite-rate chemistry calculations require the use of an appropriate mechanism that can be large (a few hundred reactions and species) even for simple hydrocarbons and can present serious computational challenges. For instance, Prager et al. [13] used a mechanism consisting of 275 reactions and 49 species to model lean/stoichiometric methane-air flames while Starik and Titova [14] proposed an ionic mechanism containing 392 reactions and 59 species to predict the

ion concentrations in a perfectly stirred reactor. Use of such large mechanisms requires considerable computational resources, in terms of both hardware and wall-time, and hence precludes their use in multi-dimensional reacting flow simulations for design/developmental studies. Equilibrium chemistry computations assume that the reactions occur at time scales much shorter than the flow (mixing and/or diffusion) time scale; and the concentration of the final products depends only on the temperature, pressure, and initial elemental mixture composition of the system. Approximately 30 species (including ions and electrons) are usually adequate for describing the combustion products required for engineering design and analyses of most fuel-air combustion systems. The concentrations of species in the mixture are computed using thermophysical properties (enthalpy, entropy, Gibbs free energy) of the system. These thermophysical properties can be computed using constants that are easily available (for instance, in the CHEMKIN and NASA-CEA databases). Finite-rate chemistry computations, on the other hand, require reaction rate constants for each elementary reaction in the mechanism. These reaction rates constants are not readily available, especially for elementary reactions involving electrons and charges species. Equilibrium chemistry computations, especially for hydrocarbon-air combustions, are also “extendible” in that equilibrium concentrations for any hydrocarbon-air combustion can be obtained by merely replacing the thermophysical constants of one hydrocarbon with another with all other species remaining the same. Finite-rate chemistry computations, on the other hand, would require a different mechanism with the inclusion of more intermediate species to compute the species concentrations. Given these considerations, equilibrium calculations can provide valuable estimates of charged species concentrations in plasma-based engineering systems characterized by large Damkohler numbers at greatly reduced computational cost and effort.

To this end, we conducted a systematic study of the problem of computing equilibrium concentrations of various neutrals and ions in combusting stoichiometric hydrocarbon-air mixtures under various conditions of temperature, pressure, and thermal disequilibrium. While the identity of dominant charged species in hydrocarbon flames is well-established in laboratory and low-pressure flames using finite-rate chemistry calculations, our goal is to answer the following questions with regard to the equilibrium calculations conducted by Calcote and King and assess the suitability of the use of equilibrium chemistry computations for engineering applications in power generating equipment.

- (1) Can a more accurate method to compute equilibrium concentrations of all ions and neutrals considered in Calcote's original analyses yield a value of the magnitude of the dominant charged specie which is closer to ion concentrations estimated from experimental data?
- (2) What is the impact of mixture composition (considering a different set of neutral and charged species as combustion products) on the magnitude of the dominant charged specie?

- (3) What is the impact of elevated electron temperature (thermal non-equilibrium) on the equilibrium concentration of charged species in hydrocarbon combustion?

Our computations seek to determine whether equilibrium chemistry calculations conducted with the inclusion of H_3O^+ ions and the effect of elevated electron temperatures can indeed yield results consistent with experimental observations, as postulated by Calcote and King. Furthermore, the validity of equilibrium computations at higher pressures and thermal disequilibrium is also investigated. To the best of the author's knowledge, such a systematic study has not been conducted.

This paper is organized as follows. Section 2 describes the method of solution, and Section 3 discusses the results. Section 4 briefly summarizes the main findings of this work.

2. Method of Solution

The equilibrium concentrations of charged and neutral species were obtained by using the Chemical Equilibrium Analysis (CEA) code. The CEA code computes equilibrium concentrations by minimizing the Gibbs free energy of the system containing all the ions and neutral species assumed to be present in the system. Details of the computational methodology can be obtained from [20]. The CEA code is well-validated and widely used for equilibrium computations and hence used in this study. The neutral and charged species originally considered by Calcote (namely, H_2 , N_2 , CO , CO_2 , H , OH , O , H_2O , O_2 , NO , Na , C , H_2^+ , N_2^+ , CO^+ , CO_2^+ , H^+ , OH^+ , O^+ , H_2O^+ , O_2^+ , NO^+ , Na^+ , C^+ , and e^-) were used to obtain the equilibrium concentrations of a stoichiometric propane-air mixture at $T = 2200$ K and $P = 1$ atm using the CEA code. This set of neutral and charged species used by Calcote will be referred to as mixture I henceforth. The equilibrium concentrations obtained by using the CEA code were compared with those obtained by using the Calcote method [10]. Equilibrium computations of two other propane-air mixtures consisting of different sets of ions and neutrals than those used by Calcote were conducted to assess the impact of mixture composition on the dominant charged species concentration. The first propane-air mixture considered in this study, referred to as mixture II, had 18 neutral and 7 charged species. The neutral species in mixture II were C_3H_8 (propane), O_2 , CO_2 , H_2O , N_2 , N , O , NO , OH , H , N_2O , CO , H_2 , NO_2 , HO_2 , C_2H_2 , C , and CH . The seven charged species in mixture II were CHO^+ , e^- , H_3O^+ , NO^+ , O_2^- , O^- , and OH^- . The neutral and charged species assumed to be present in mixture II have shown good agreement with measured ion currents in constant volume cylinders and internal combustion engines, as discussed in [17, 18] and hence used in this study. Validation of the ion current predictions in a constant volume methane-air mixture using mixture II (as discussed in [17]) is shown in Section 3.4 for the benefit of the reader.

For the sake of completeness, equilibrium composition of a stoichiometric propane-air mixture including all the species in mixture I and mixture II, termed as mixture III was also studied. The species present in mixture III were

TABLE 1: Comparison of equilibrium concentrations (Calcote and CEA).

Species	Calcote (#/cc)	CEA (#/cc)
H ₂	8.2x10 ¹⁵	8.4x10 ¹⁵
N ₂	2.4x10 ¹⁸	2.4x10 ¹⁸
CO	3.3x10 ¹⁶	3.1x10 ¹⁶
CO ₂	3.5x10 ¹⁷	3.5x10 ¹⁷
H	9.2x10 ¹⁵	9.4x10 ¹⁵
OH	7.9x10 ¹⁵	8.6x10 ¹⁵
O	6.6x10 ¹⁴	6.0x10 ¹⁴
H ₂ O	5.0x10 ¹⁷	5.0x10 ¹⁷
O ₂	1.5x10 ¹⁵	1.5x10 ¹⁵
NO	6.3x10 ¹⁵	5.9x10 ¹⁵
NO ⁺	1.7x10 ⁷	1.8x10 ⁷

C₃H₈ H₂ N₂ CO CO₂ H OH O H₂O O₂ CH NO H₂⁺ N₂⁺ CO⁺ CO₂⁺ H⁺ OH⁺ O⁺ H₂O⁺ O₂⁺ CH⁺ NO⁺ e⁻ N N₂O NO₂ HO₂ C₂H₂, C HCO⁺ H₃O⁺ O₂⁻ O⁻ OH⁻. Positively charged species, namely, H₂⁺ N₂⁺ CO⁺ CO₂⁺ H⁺ OH⁺ O⁺ H₂O⁺ O₂⁺ CH⁺ from Calcote's original calculations, were included in this mixture. The effect of elevated electron temperature was studied by using the method of equilibrium constants as described in detail in Section 3.4.

3. Results and Discussions

This section discusses the equilibrium concentration of ions and neutrals in a stoichiometric premixed propane-air mixture using different computations methods (CEA and Calcote), mixture compositions (mixture I, mixture II, and mixture III), and electron temperatures. Additionally, the effects of gas temperature and pressure for engine-like conditions are also discussed.

3.1. Comparison of CEA Calculations with the Calcote Method (Code Validation). There are no detailed experiments reporting the temperature and concentrations of ions and neutral species in stoichiometric propane-air flames at ambient pressure (Calcote's conditions) and hence it is not possible to compare the numerical results presented by Calcote (see Table 1 in [10]) with experimental data. For the sake of validation, equilibrium concentrations were computed using the Calcote method with the CEA code. Following the Calcote method, the equilibrium mixture composition of the most dominant ion, NO⁺, was computed considering only NO⁺ and e⁻ as the charged species, along with other neutral species considered by Calcote (H₂, N₂, CO, CO₂, H, OH, O, H₂O, O₂, and NO). These computations were conducted with a stoichiometric propane-air mixture at 2200 K and 1 atm, as reported in [10]. Table 1 shows a comparison of the important charged and neutral species. The equilibrium concentrations computed with the CEA code compares very well with those reported in [10] and hence serves as a validation of the computational methodology used in this work. It was verified

TABLE 2: Comparison of the dominant equilibrium ion concentrations using the Calcote method and minimization of the Gibbs free energy method.

Species	Calcote (ions/cc)	CEA (all species) (ions/cc)
NO ⁺	1.7x10 ⁷	1.8x10 ⁷
H ₂ O ⁺	4.4x10 ⁴	4.02x10 ²
O ₂ ⁺	2.2x10 ⁴	8.4x10 ¹
CO ₂ ⁺	1.5x10 ³	2

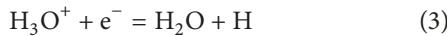
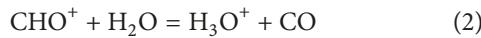
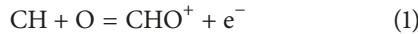
that the concentrations of other charged species (such as H₂O⁺, H₂⁺ etc.) were the same as those reported in [10] using the Calcote method.

3.2. Equilibrium Computations considering All of Calcote's Ions and Neutrals Simultaneously. Equilibrium concentrations of a stoichiometric propane-air mixture at T = 2200 K and P = 1 atm were obtained by minimizing the Gibbs free energy of a system consisting of all the ions and neutrals considered in Calcote's study (mixture I). This method of computing the equilibrium concentrations is more accurate than the Calcote method. Table 2 shows a comparison between the equilibrium concentrations of the dominant ions using the Calcote method and the CEA code considering all species together. It is seen that the peak concentration of the dominant ion, namely, NO⁺ predicted by Calcote is nearly the same as that predicted by the CEA code. Moreover, both methods predict the same four most dominant ions, namely, CO₂⁺, O₂⁺, H₂O⁺ and NO⁺; and both predict that NO⁺ >> H₂O⁺ (which is the second most dominant positive ion). Hence the total ion concentration is determined solely by NO⁺ and the contribution of other ions to the total ion concentration is insignificant in results obtained by both methods. Table 2 also shows that the ion concentrations of CO₂⁺, O₂⁺, and H₂O⁺ predicted by the CEA code are two to three orders of magnitude less than those predicted by Calcote's method. This difference is due to the method of computation of the equilibrium concentrations. As explained earlier, the Calcote method computed equilibrium concentrations by assuming that only a single ion was present in the mixture while the CEA method obtains the equilibrium concentrations using a more rigorous and accurate method, by minimizing the Gibbs free energy of the entire system under consideration. There are no detailed experiments reporting the measured concentrations of ions such as H₂O⁺, O₂⁺, and CO₂⁺ in stoichiometric propane-air flames at ambient pressure and hence it is not possible to compare the numerical results with experimental data. However, for most engineering applications, the peak ion concentration is of primary importance. The more accurate calculations using the CEA code show that the main conclusion in [10], namely, that, in a stoichiometric propane-air mixture at T = 2200 K and P = 1 atm, NO⁺ is the dominant ion with an ion concentration of $\sim 10^7$ ions/cc, is still valid.

TABLE 3: Comparison of equilibrium concentrations of the dominant ions in mixtures I–III.

Species	Mixture I	Mixture II	Mixture III
NO^+	1.7×10^7	1.8×10^7	1.78×10^7
H_3O^+	-	3.06×10^6	3.05×10^6
HCO^+	-	1.03×10^3	1.03×10^3

3.3. Equilibrium Computations including the Effects of Negative Ions and H_3O^+ . Calcote and King considered only positive ions formed by thermal ionization in their equilibrium calculations. In contrast, Green and Sugden [9] proposed that the elementary reactions responsible for ionization in hydrocarbon flames were as follows:



Chemi-ions such as CHO^+ and H_3O^+ were not considered in Calcote's computation. The impact of the equilibrium mixture composition on the identity and magnitude of the most dominant charged species was assessed by using different sets of ions and neutrals, namely, mixtures II and III. The equilibrium composition of mixtures II and III were also computed at $T = 2200$ K and 1 atm for a stoichiometric propane-air mixture using the CEA code. Table 3 shows a comparison of the equilibrium concentrations of the dominant ions in mixtures I, II, and III. It is seen that NO^+ is the most dominant ion in mixtures II and III as reported by Calcote (for mixture I). Furthermore, the concentration of NO^+ for all three mixtures was between 1.7×10^7 and 1.8×10^7 . The ion concentration of NO^+ in mixtures II and III compares well (~5.5% higher) with the ion concentration of 1.7×10^7 ions/cc reported by Calcote and King.

H_3O^+ was the second most dominant ion in mixtures II and III (mixture I did not include chemi-ions) and its concentration was $\sim 3.06 \times 10^6$ ions/cc, which is considerably lower than the ion concentration of NO^+ . The results obtained by using the CEA code demonstrate that neither the method of solution nor the mixture composition has a significant impact on the identity of the most dominant ion (NO^+) and its concentration ($\sim 1.7 \times 10^7$) in laboratory stoichiometric propane-air flames at ambient pressure ($P = 1$ atm). Results presented in Sections 3.1–3.3 show that, even with the inclusion of chemi-ions (such as H_3O^+ and HCO^+), the peak ion concentrations observed experimentally cannot be explained under conditions of thermal equilibrium between the electrons and heavy particles (ions and neutrals).

3.4. Effect of Thermal Non-Equilibrium (Elevated Electron Temperature) on the Charged Species Concentrations. The effect of elevated electron temperature on increasing the ion concentration in hydrocarbon flames is well known [21]. The CEA code does not compute equilibrium concentrations under conditions of thermal disequilibrium hence an in-house solver based on the equilibrium constant method was used to study the effect of elevated electron temperature on

the equilibrium concentration of charged species in reacting mixture II. Furthermore, the equilibrium constant method makes it easier to explain the impact of electron temperature on charged species concentrations since the equilibrium constants are functions of temperature.

Chemical equilibrium can be described by two equivalent formulations, namely, the equilibrium constant method and minimization of the free energy [20]. The methodology for computing equilibrium concentrations using the minimization of the free energy is described in detail in [20]. Details of the equilibrium constant method are described briefly next for the benefit of the reader (additional details are described in [17, 18]).

3.4.1. Equilibrium Constant Method. Consider a mixture of N distinct species in equilibrium in a reacting mixture under a given set of thermodynamic conditions. Let the N species be composed on M chemical elements. To obtain the equilibrium concentrations of these N species, a system of equations consisting of M linear element-conservation relations and $N-M$ nonlinear equilibrium equations is required. For systems with charged species, an additional charge conservation equation is also needed; hence $N-M-1$ non-linear equilibrium equations are needed.

An elementary reaction (reversible or irreversible) involving the N chemical species can be written in the general form as

$$\sum_{k=1}^N a_{ks} X_k \iff \sum_{k=1}^N b_{ks} X_k \quad (4)$$

where a_{ks} and b_{ks} are integer numbers representing stoichiometric coefficients of species k in reaction s ($1, \dots, N-M$) and X_k is the chemical symbol for the k^{th} species.

The equilibrium relation for reaction s can be written as

$$k_s R_s = P_s, \quad (5)$$

where

$$R_s = \prod_k [c_k]^{a_{ks}} ; \quad (6)$$

$$P_s = \prod_k [c_k]^{b_{ks}},$$

k_s is the equilibrium constant of reaction s and $[c_k]$ is the molar concentration of species k .

The linear element-conservation equations are of the form ($i = 1, M$):

$$\sum_{k=1}^N d_{ki} X_k = C_i \quad (7)$$

TABLE 4: Validation of equilibrium constant method with CEA code.

No.	Species	Minimization of Gibbs Free Energy (CEA code) Mole fractions	Equilibrium Constant method Mole fractions
1	O ₂	4.46 x 10 ⁻³	4.45 x 10 ⁻³
2	CO ₂	1.05 x 10 ⁻¹	1.06 x 10 ⁻¹
3	NO	1.76 x 10 ⁻³	1.85 x 10 ⁻³
4	H ₂	2.54 x 10 ⁻³	2.55 x 10 ⁻³
5	NO ⁺	5.35 x 10 ⁻¹²	5.06 x 10 ⁻¹²
6	OH ⁻	3.91 x 10 ⁻¹³	3.83 x 10 ⁻¹³
7	O ⁻	1.05 x 10 ⁻¹⁴	1.14 x 10 ⁻¹⁴

where C_i is the initial number of atoms of element i and d_{ki} is the number of atoms of element i in species X_k . For instance, in species CO₂, $d = 1$ for C and $d = 2$ for O₂.

The equilibrium constant for a given reaction s is computed using the treatment outlined in standard thermodynamic textbooks as

$$\ln k_s = \frac{\Delta S_s^\circ(T)}{R} - \frac{\Delta H_s^\circ(T)}{RT} \quad (8)$$

where Δ refers to the change in entropy and enthalpy in passing from reactants to products in a given reaction s , R is the universal gas constant, and T is the temperature. Thus, the terms in the RHS of (8) can be expressed as

$$\frac{\Delta S_s^\circ(T)}{R} = \sum_{k=1}^N v_{ks} \frac{S_k^\circ(T)}{R} \quad (9)$$

$$\frac{\Delta H_s^\circ(T)}{RT} = \sum_{k=1}^N v_{ks} \frac{H_k^\circ(T)}{RT} \quad (10)$$

where v_{ks} is the difference between the stoichiometric coefficients of products and reactants of a given species in reaction s .

$$v_{ks} = b_{ks} - a_{ks} \quad (11)$$

The specific enthalpy and entropy of species k required for evaluating (9) and (10) were computed by using polynomials as shown in (12) and (13) (as discussed in [22]). The polynomial coefficients in (12) and (13) were obtained from the CHEMKIN database.

$$H_k = \left(a_{1,k} + \frac{a_{2,k}}{2}T + \frac{a_{3,k}}{3}T^2 + \frac{a_{4,k}}{4}T^3 + \frac{a_{5,k}}{5}T^4 + \frac{a_{6,k}}{T} \right) RT \quad (12)$$

$$S_k = \left(a_{1,k} \ln T + a_{2,k}T + \frac{a_{3,k}}{2}T^2 + \frac{a_{4,k}}{3}T^3 + \frac{a_{5,k}}{4}T^4 + a_{7,k} \right) R \quad (13)$$

In this work, the number of species, N = 25 (including ions) and number of elements, M = 4. Hence, to compute the

equilibrium concentrations of the 25 species, one requires 4 element balance equations, 1 charge balance equation, and 20 nonlinear equilibrium equations. The set of species, and nonlinear equilibrium equations used in this work are as shown in Tables 6 and 7, respectively, in Appendix. The linear equations describing element and charge conservation are also shown in Appendix.

3.4.2. Validation of the In-House Solver Using the Equilibrium Constant Method. The solver used to compute the equilibrium concentrations of species in mixture II has been well-validated with results from the CEA code and experimental data. Table 4 compares the equilibrium mole fractions of important charged and neutral species in a stoichiometric propane-air mixture at T = 2200 K and P = 1 atm. It is seen that the species mole fractions predicted by the in-house solver based on the equilibrium constant method compares well with those predicted by the CEA code based on the method of minimization of the Gibbs free energy.

As further validation, the solver results were also compared with experimental data. Figure 1 shows a comparison of the computed ion current with experimental data in a constant volume cylinder consisting of a methane-air mixture for two different air-fuel ratios (AFR) [17].

It is seen that the location and the magnitude of the peak current is captured well. The ion current is overpredicted for t > 40 milliseconds since the thermal model describing the temperature variation in the cylinder was assumed to be adiabatic (for the sake of simplicity). Thus, the higher cylinder temperature due to the adiabatic assumption leads to a higher predicted ion current for t > 40 milliseconds, whereas in the actual experiment the heat loss from the cylinder would likely lead to a faster drop in the cylinder temperature and hence the ion current. The results presented in Table 4 and Figure 1 validate the in-house solver based on the equilibrium constant method used in this work. Reference [18] compares the ion current in an HCCI engine for various fuel-air mixtures with experimental data presented in [19]. It is seen that the equilibrium chemistry computations agree well with finite-rate chemistry computations presented in reference [19].

3.4.3. Effect of Elevated Electron Temperature. The effect of elevated electron temperature on the equilibrium concentration of charged species in a reacting mixture was studied by

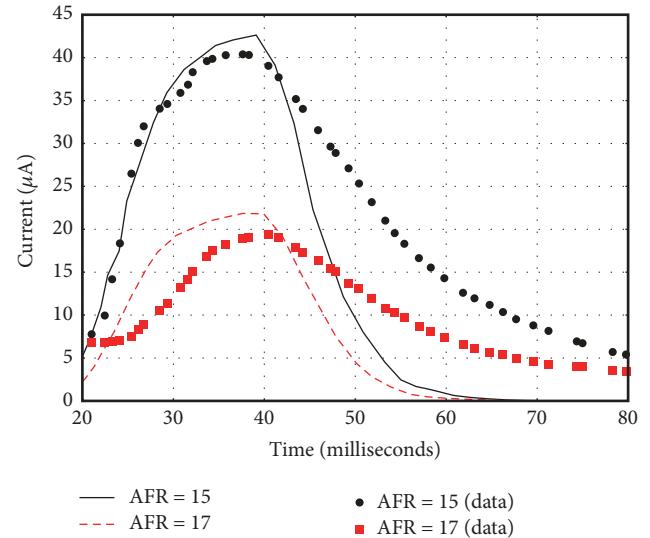
TABLE 5: Effect of T_e , T_g and pressure on equilibrium concentration of ions (mixture II) in a stoichiometric propane-air mixture.

	T_g (K)	T_e (K)	Pressure (atm)	H_3O^+ (ions/cc)	NO^+ (ions/cc)	Total (ions/cc)	Application
1	2200	2200	1	5.66×10^6	1.69×10^7	2.2×10^7	Laboratory flame (Bunsen burner) with thermal equilibrium
2	2800	2800	40	1.53×10^{10}	5.16×10^{10}	6.69×10^{10}	Burned gas conditions (engines) with thermal equilibrium
3	2800	4200 ($T_e = 1.5T_g$)	40	2.81×10^{12}	7.05×10^{10}	2.81×10^{12}	Burned gas conditions (engines) with thermal dis-equilibrium

TABLE 6: List of species.

	Species
1	C_3H_8
2	O_2
3	CO_2
4	H_2O
5	N_2
6	N
7	O
8	NO
9	OH
10	H
11	N_2O
12	CO
13	H_2
14	NO_2
15	HO_2
16	C_2H_2
17	C
18	CH
19	HCO^+
20	e^-
21	H_3O^+
22	NO^+
23	O_2^-
24	O^-
25	OH^-

computing the equilibrium constants of reactions involving electrons at the elevated electron temperature whereas the equilibrium constants of all the other reactions were computed at the gas temperature. Hence, equilibrium constants of reactions 15-18 and reaction 20 shown in Table 6 were computed at the assumed electron temperature using Eq. (8). This procedure is equivalent to the formulation described

FIGURE 1: Comparison of the computed ion current with experimental data in a constant volume cylinder (CH_4 -air mixture, air-fuel ratio (AFR) = 15 & 17) [17].

in Ref. [23] to compute the equilibrium concentration for a system with multiple gas temperatures.

Figure 2 shows the effect of electron temperature (T_e) on the concentration (ions/cc) of H_3O^+ and NO^+ . One can see that as the degree of disequilibrium increases from $T_e = T_g = 2200$ K to $T_e = 5,000$ K and $T_g = 2200$ K, the concentration of NO^+ increases by 30%, whereas that of H_3O^+ increases by about 4 orders of magnitude. At $T_e \sim 3700$ K, or $T_e \sim 1.7T_g$, the concentration of H_3O^+ is approximately 1.4×10^{10} ions/cc, which is close to the experimental value reported by Goodings et al. [11].

Figure 2 shows that inclusion of H_3O^+ in the equilibrium mixture and elevated electron temperature can yield positive ion concentration comparable to those observed in laboratory flame experiments. At $T = 2200$ K, the H_3O^+ ion concentration is below that of NO^+ as stated earlier and its

TABLE 7: List of reactions.

1	$\frac{1}{2}H_2 = H$	$k_1 = \frac{[H]}{[H_2]^{0.5}} \sqrt{P}$
2	$\frac{1}{2}O_2 = O$	$k_2 = \frac{[O]}{[O_2]^{0.5}} \sqrt{P}$
3	$\frac{1}{2}N_2 = N$	$k_3 = \frac{[N]}{[N_2]^{0.5}} \sqrt{P}$
4	$\frac{1}{2}H_2 + \frac{1}{2}O_2 = OH$	$k_4 = \frac{[OH]}{[H_2]^{0.5} [O]^{0.5}}$
5	$\frac{1}{2}N_2 + \frac{1}{2}O_2 = NO$	$k_5 = \frac{[NO]}{[N_2]^{0.5} [O]^{0.5}}$
6	$H_2 + \frac{1}{2}O_2 = H_2O$	$k_6 = \frac{[H_2O]}{[H_2] [O_2]^{0.5}} (P)^{-0.5}$
7	$CO + \frac{1}{2}O_2 = CO_2$	$k_7 = \frac{[CO_2]}{[CO] [O_2]^{0.5}} (P)^{-0.5}$
8	$NO + \frac{1}{2}O_2 = NO_2$	$k_8 = \frac{[NO_2]}{[NO] [O_2]^{0.5}} (P)^{-0.5}$
9	$O_2 + \frac{1}{2}H_2 = HO_2$	$k_9 = \frac{[HO_2]}{[O_2] [H_2]^{0.5}} (P)^{-0.5}$
10	$N_2 + \frac{1}{2}O_2 = N_2O$	$k_{10} = \frac{[N_2O]}{[N_2] [O_2]^{0.5}} (P)^{-0.5}$
11	$C_xH_y + \left(x + \frac{y}{4}\right)O_2 = xCO_2 + \frac{y}{2}H_2O$	$k_{11} = \frac{[CO_2]^{(x)} [H_2O]^{(y/2)}}{[C_xH_y] [O_2]^{(x+y/4)}} (P)^{(y/2-1)}$
12	$C_xH_y = C_xH_{y-1} + H$	$k_{12} = \frac{[C_xH_{y-1}] [H]}{[C_xH_y]} P$
13	$C_2H_2 = 2C + H_2$	$k_{13} = \frac{[C]^2 [H_2]}{[C_2H_2]} P^2$
14	$CO + OH = CH + O_2$	$k_{14} = \frac{[CH] [O_2]}{[CO] [OH]}$
15	$CH + O = HCO^+ + e^-$	$k_{15} = \frac{[HCO^+] [e^-]}{[CH] [O]}$
16	$N + O = NO^+ + e^-$	$k_{16} = \frac{[NO^+] [e^-]}{[N] [O]}$
17	$H_3O^+ + e^- = H_2O + H$	$k_{17} = \frac{[H_2O] [H]}{[H_3O^+] [e^-]}$
18	$O_2 + e^- = O_2^-$	$k_{18} = \frac{[\bar{O}_2^-]}{[O_2] [e^-]} P^{-1}$
19	$O + O_2^- = O_2 + O^-$	$k_{19} = \frac{[O_2] [O^-]}{[O] [O_2^-]}$
20	$OH + e^- = OH^-$	$k_{20} = \frac{[OH^-]}{[OH] [e^-]} P^{-1}$

concentration is $\sim 10^7$ as noted by Calcote. Figure 2 also shows that, in the absence of H_3O^+ , the high values of ion concentration in flames cannot be explained by NO^+ concentration alone, even at elevated electron temperatures. Figure 2 thus shows the equilibrium calculations which include chemi-ions (H_3O^+) at slightly elevated electron temperature ($T_e \sim 1.7T_g$) can yield ion concentrations comparable to experiments conducted on laboratory flames, thus confirming the conclusions by Calcote and King.

The sharp increase in H_3O^+ with elevated electron temperature as compared to NO^+ can be explained by examining the effect of temperature on the equilibrium constants of the reactions $N + O \rightleftharpoons NO^+ + e^-$ and $H_2O + H \rightleftharpoons H_3O^+$

+ e^- (reactions 16 and 17 in Table 7). Figure 3 shows the variation of the equilibrium constant for reactions 16 and 17 as a function of temperature. It is seen that the equilibrium constant of reaction 17 drops by about 10 orders of magnitude whereas that of reaction 16 increases by about 4 orders of magnitude for $2000 \text{ K} < T_e < 5000 \text{ K}$. The stronger temperature dependence of reaction 17 yields a markedly higher concentration of H_3O^+ compared to NO^+ with increase in electron temperatures.

3.5. Effect of Flame Temperature and Pressure on the Charged Species Computations. The discussion in Section 3.4 showed that ion concentrations in laboratory flames can be explained

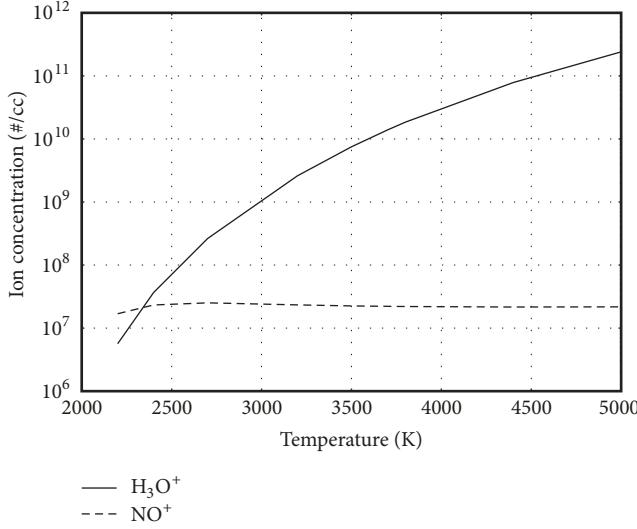


FIGURE 2: Effect of electron temperature (T_e) on the concentration (ions/cc) of H_3O^+ and NO^+ under laboratory flame conditions ($P = 1$ atm) for a stoichiometric propane-air mixture.

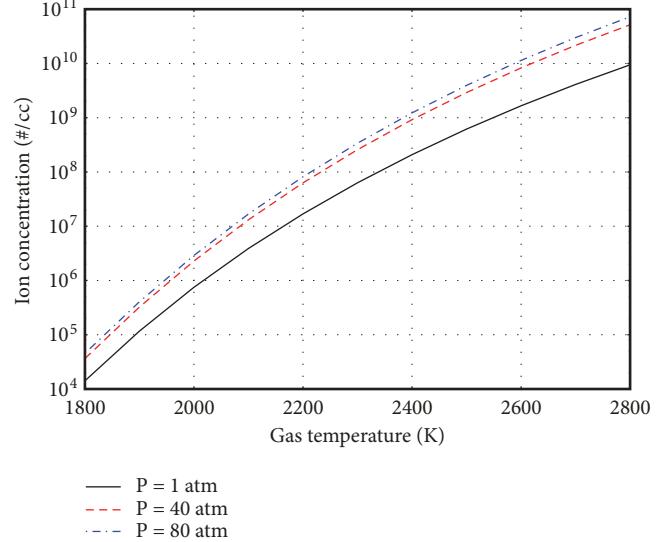


FIGURE 4: Effect of gas temperature on NO^+ ion concentration for $P = 1, 40$ and 80 atm under conditions of thermal equilibrium ($T_e = T_g$) in a stoichiometric propane-air mixture.

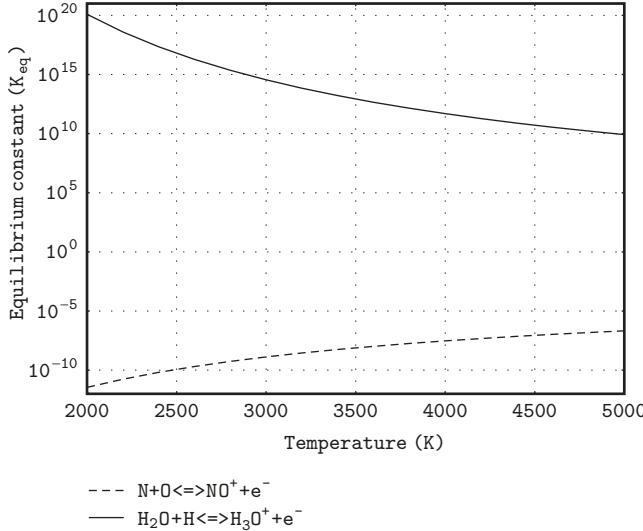


FIGURE 3: Effect of electron temperature (T_e) on the equilibrium constants of H_3O^+ and NO^+ .

by assuming the presence of chemi-ions (H_3O^+) and thermal disequilibrium. The concentration of charged species, however, is also strongly dependent on the flame temperature (or gas temperature) and pressure. Calcote's equilibrium calculation were for a typical laboratory flame such as a Bunsen burner operating at 1 atmosphere with $T_g = 2200\text{K}$. In typical energy conversion devices such as automotive engines and gas turbines, the combustion reactants (fuel/air mixture) are preheated and combustion takes place at higher temperatures and pressures. For instance, in an internal combustion engine, the fuel-air mixture in the engine cylinder is heated to $\sim 600 - 650$ K during the isentropic compression before the ignition begins. The unburned fuel-air mixture in the cylinder is typically between 20 and 40 atm (depending on the

compression ratio and boost pressure) just prior to ignition. The burned gas temperature and pressure near top-dead-center (TDC) can be close to 2800 K and 80 atm (or higher), respectively. Under these conditions, the electron and gas temperatures can be in local thermodynamic equilibrium (LTE) or $T_e \sim T_g$. The higher collision frequency at these temperature and pressure conditions reduces the thermal disequilibrium (locally) between the electron temperature and gas temperature (see Figure 2 in [24]). Table 5 shows the effect of T_e , T_g , and pressure on equilibrium concentration of the dominant ions, NO^+ and H_3O^+ , for mixture II. One can see a marked increase in the charged species concentration under engine-like conditions as compared to the laboratory flame under thermal equilibrium conditions ($T_g = T_e = 2200$ K and $P = 1$ atm). The increase in the chemi-ion concentration of H_3O^+ is pronounced even with a slight degree of thermal disequilibrium between electron and gas temperatures. The equilibrium composition of charged species under thermal equilibrium conditions are consistent with experimentally measured ion currents in a constant volume chamber and internal combustion engines as shown in [17, 18].

These results suggest that under engine-like conditions at higher temperatures and pressures, ion concentrations at the flame front can be explained by the presence of H_3O^+ under thermal equilibrium or slight thermal disequilibrium.

Figures 4 and 5 show the effect of gas temperature and pressure on NO^+ and H_3O^+ , respectively, for a range of engine-like temperatures under conditions of thermal equilibrium ($T_e = T_g$). The temperature range, $1800\text{ K} < T_g < 2800\text{ K}$ was chosen since it is representative of the burned gas temperature in engines during the combustion process. The pressures, $P = 40$ atm and $P = 80$ atm, are representative values at start of ignition and peak pressure in an engine. Results for $P = 1$ atm represent the engine pressure at the bottom dead center (BDC) and is shown as a baseline case.

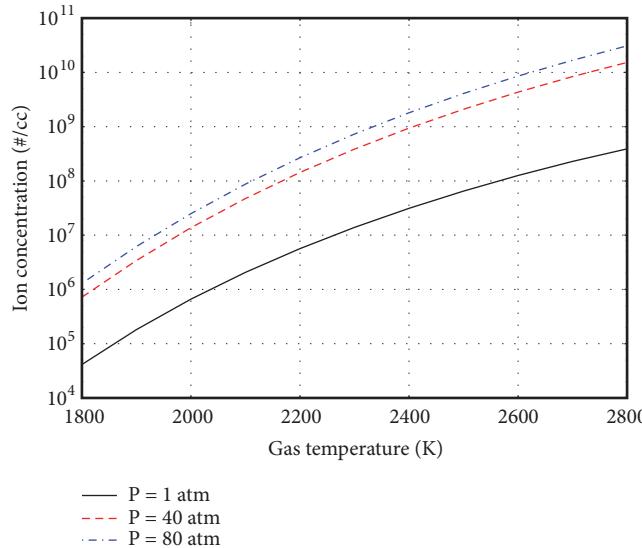


FIGURE 5: Effect of gas temperature on H_3O^+ ion concentration for $P = 1, 40$ and 80 atm under conditions of thermal equilibrium ($T_e = T_g$) in a stoichiometric propane-air mixture.

Figures 4 and 5 show that gas temperature has a strong impact on the ion concentration for both NO^+ and H_3O^+ over the temperature and pressure range considered in this work. It is seen that ion concentrations increase by 4-5 orders of magnitude at $T = 2800$ K as compared to their values at $T = 1800$ K. It is also seen that a given temperature, there is about 1-2 orders of magnitude increase in ion concentration between $P = 1$ atm and $P = 40$ atm, whereas the increase in ion concentrations between $P = 40$ atm and $P = 80$ atm is not as pronounced. Figure 3 showed the marked effect of temperature on the equilibrium constants for the reactions $\text{N} + \text{O} \rightleftharpoons \text{NO}^+ + \text{e}^-$ and $\text{H}_2\text{O} + \text{H} \rightleftharpoons \text{H}_3\text{O}^+ + \text{e}^-$ which also explains the trends shown in Figures 4 and 5.

4. Conclusions

The equilibrium computations conducted by Calcote and King for charged species concentrations in laboratory hydrocarbon flames were extended to include the effects of chemi-ions and thermal disequilibrium. This study also evaluated the effect of computational methodology and mixture composition on the charged species computations. The study verified that more detailed and accurate equilibrium computations with the inclusion of chemi-ions yield ion concentrations similar to those reported by Calcote when the electron temperature was assumed equal to the gas temperature for a laboratory flame with $T_g = 2200$ and $P = 1$ atm. Equilibrium compositions of a stoichiometric propane-air mixture showed a marked increase in the concentration of H_3O^+ ions at elevated electron temperatures. However, no significant increase in the NO^+ concentration was noted with increased electron temperatures. These equilibrium computation results validate the conclusions of Calcote and King, namely, that for a laboratory flame, thermal equilibrium does not exist between species in the flame front and that ions are

produced not by thermal process but by chemi-ionization. The equilibrium computations under engine-like conditions showed a marked increase in the ion concentration of H_3O^+ with and without the assumption of LTE. Equilibrium computations using a reduced set of charged and neutral species (as in mixture II) which include the dominant chemi-ion, namely, H_3O^+ , can provide useful estimates of charged species concentrations in modern combustion devices.

Appendix

See Tables 6 and 7.

The element balance equations of C, H, O, and N can be written as follows:

$$\begin{aligned} N_c &= xN_{\text{fuel}} + N_{\text{CO}_2} + N_{\text{CO}} + xN_{\text{CxHy-1}} + N_{\text{C}} \\ &\quad + 2N_{\text{C}_2\text{H}_2} + N_{\text{CH}} + N_{\text{HCO}_+} \\ N_h &= yN_{\text{fuel}} + 2N_{\text{H}_2\text{O}} + N_{\text{OH}} + N_{\text{H}} + 2N_{\text{H}_2} + N_{\text{HO}_2} \\ &\quad + (y-1)N_{\text{CxHy-1}} + 2N_{\text{C}_2\text{H}_2} + N_{\text{CH}} + N_{\text{HCO}_+} \\ &\quad + 3N_{\text{H}_3\text{O}^+} + N_{\text{OH}^-} \end{aligned} \quad (\text{A.1})$$

$$\begin{aligned} N_o &= 2N_{\text{O}_2} + 2N_{\text{CO}_2} + N_{\text{H}_2\text{O}} + N_{\text{O}} + N_{\text{NO}} + N_{\text{OH}} \\ &\quad + N_{\text{N}_2\text{O}} + N_{\text{CO}} + 2N_{\text{NO}_2} + 2N_{\text{HO}_2} \\ &\quad + N_{\text{HCO}_+} + N_{\text{H}_3\text{O}^+} + N_{\text{NO}_+} + 2N_{\text{O}_2^-} + N_{\text{O}_-} \\ &\quad + N_{\text{OH}^-} \end{aligned}$$

$$N_n = 2N_{\text{N}_2} + N_{\text{N}} + N_{\text{NO}} + 2N_{\text{N}_2\text{O}} + N_{\text{NO}_2} + N_{\text{NO}_+}$$

Here, N_s represents the number of moles of species N_s and N_c , N_h , N_o , and N_n are the total number of moles of C, H, O, and N, respectively, in the system under consideration.

The charge conservation equation can be written as

$$\begin{aligned} N_{\text{e}^-} + N_{\text{O}_2^-} + N_{\text{O}_-} + N_{\text{OH}^-} \\ = N_{\text{HCO}_+} + N_{\text{H}_3\text{O}^+} + N_{\text{NO}_+} \end{aligned} \quad (\text{A.2})$$

Reaction 11 in Table 7 identifies the fuel as C_xH_y ; hence one can study propane by specifying $x = 3, y = 8$.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Disclosure

The research did not receive any specific funding, but was performed as part of the employment of the author at Argonne National Laboratory.

Conflicts of Interest

The author declares that there are no conflicts of interest regarding the publication of this paper.

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