

Chemical Kinetic Modelling of Ar-CO₂ Thermal Plasmas Under Reduced Gas Pressure Conditions

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Abstract

A chemical kinetic model of Ar-CO₂ gas mixtures under thermal plasma conditions has been constructed to investigate the gas temperature dependence of ion and neutral compositions under reduced pressure conditions. Numerical results are obtained for gas temperatures from 400 to 15000 K, and pressures from 10 Torr to 760 Torr. Electron impact and thermal ionization reactions, recombination reactions, radical and ion-molecule reactions (111 reactions in total) are considered in the model. The results show that degree of ionization of the plasma is significantly affected by the pressure. The results also seem to indicate that the application of local thermodynamic equilibrium models and Saha models, which are often used for the prediction of neutral species and ionized species densities respectively, may need to be reconsidered for mixture gas conditions.

1 Introduction

Argon-molecule mixtures are commonly used under plasma conditions where it is desirable to alter the properties or composition of the gases or deposit a component of the molecular gas on a substrate. Such mixtures represent a formidable experimental and modelling challenge to investigators. The original molecules can break up and re-form into neutral or ionic atomic, di-atomic, or poly-atomic species.

2 Chemical Kinetic Model

The concentration of species found in a thermal plasma has been modeled using a coupled set of generation and loss processes as described in reference [1]. This model has been extended to consider the effects of changing the system pressure.

In all, the model accounts for 14 neutral, 24 ionization, 8 attachment, 4 dissociation, 17 recombination, and 44 ion-molecule reactions. Details of the argon model

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used can be found in reference [2]. It is assumed the plasma is in dynamic equilibrium in an infinite cylindrical geometry. Diffusion of species to the cavity walls has been accounted for.

Ionic species considered in this model are Ar^+ , Ar_2^+ , C^+ , CArO^+ , CO^+ , CO_2^+ , CO_4^+ , C_2O_2^+ , O^+ , O_2^+ , O_4^+ , O_5^+ , CO_3^- , CO_4^- , O^- , O_2^- , O_3^- and electrons. Neutral species which have been considered are Ar, Ar^* , Ar^{**} , C, CO, CO_2 , O, O_2 and O_3 .

3 Model Results at Reduced Pressures

Gas temperature effects of an Ar-10% CO_2 plasma at 760 Torr pressure have already been described in reference [1]. The same basic principles also apply to the results of the model at reduced gas pressures.

To illustrate the pressure trends exhibited by the model, results were calculated at pressures of 760, 100 and 10 Torr with the electron temperature equal to the gas temperature ($T_e = T_g$). Sample results for neutral species, positive ions and negative ions are shown in Figures 1, 2, and 3 respectively at a pressure of 10 Torr.

As shown in figure 1, the chemical kinetic model exhibits 3 temperature ranges over which different species are the dominant species: range 1 Ar, CO_2 , and CO dominant, range 2 Ar, CO, and O dominant, and range 3 Ar, C, and O dominant. The use of the word range in this paper refers to the above defined ranges.

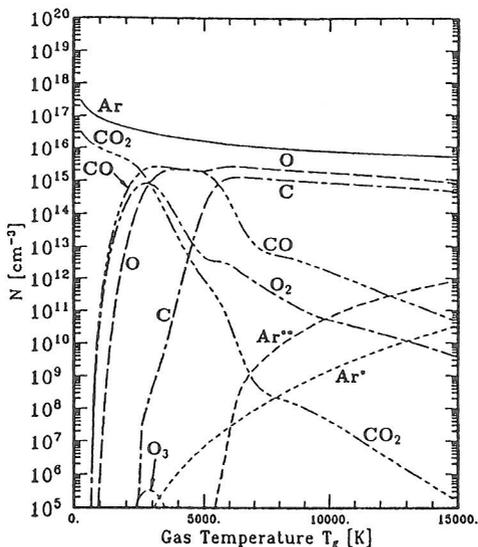


Figure 1: Neutral species concentrations as a function of gas temperature for an Ar-10% CO_2 mixture with $p = 10$ Torr, and $T_e = T_g$.

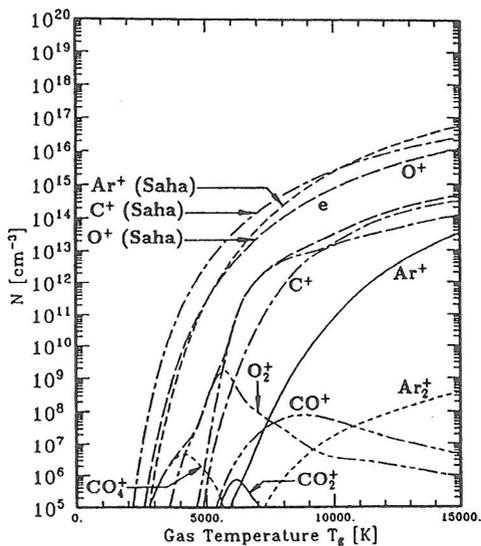


Figure 2: Positive ion concentrations as a function of gas temperature for an Ar-10%CO₂ mixture with $p = 10$ Torr, and $T_e = T_g$.

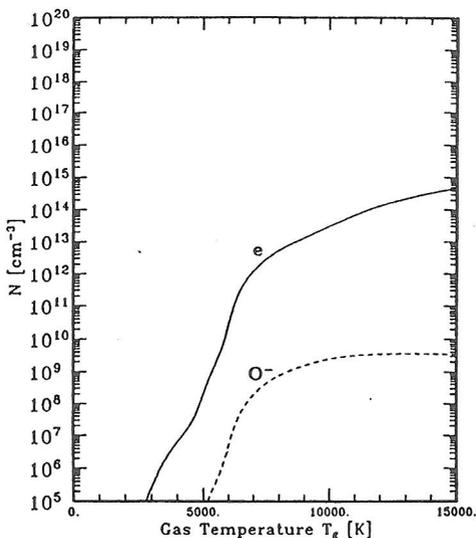


Figure 3: Negative ion concentrations as a function of gas temperature for an Ar-10%CO₂ mixture, with $p = 10$ Torr, and $T_e = T_g$.

Table 1: Temperature ranges in the Ar-10%CO₂ model, p=10–760 Torr, T_e=T_g.

Pressure [Torr]	range 1	range 2	range 3
760	≤ 3800 K	3800–6800 K	≥ 6800
100	≤ 3200 K	3200–6100 K	≥ 6100
10	≤ 2900 K	2900–5600 K	≥ 5600

Table 2: Dominant positive ions in the Ar-10%CO₂ model, T_e=T_g, p=10–760 Torr.

Pressure [Torr]	Dominant Positive Ions			
	CO ₄ ⁺	O ₂ ⁺	O ⁺	C ⁺
760	≤ 6000 K	6000–7000 K	7000–11000 K	≥ 11000
100	≤ 5100 K	5100–6300 K	6300–10200 K	≥ 10200
10	≤ 4200 K	4200–5600 K	K ≥ 5600	–

Aside from the overall reduction of all species concentrations due to the reduction of the system pressure, a comparison of the species concentrations shown in figures 1–3 with those those at atmospheric pressure shown in reference [1] indicates that the temperatures at which the transitions between ranges occurs has also been decreased. As summarized in Table 1, the transition temperature from range 1 to range 2 has decreased to from 3800 K at atmospheric pressure to 2900 K at a pressure of 10 Torr. Similarly, the transition temperature from range 2 to range 3 has decreased from 6800 K at atmospheric pressure to 5600 K at a pressure of 10 Torr. This trend can also be clearly seen in figure 4 which summarizes the the neutral species concentrations and the plasma density (as represented by the electron concentration) for pressures between 10 Torr and 760 Torr. In order to maintain the clarity of the figure, only CO₂, CO, C, and O neutral species concentrations have been included. The temperatures at which the transitions between ranges 1 and 2 and ranges 2 and 3 occur have been indicated to give an impression of the manner in which these temperatures change in response to changes in pressure.

As shown in figures 2, and 3, a decrease in pressure also causes the temperature dependent concentrations of positively and negatively charged species to decrease. The temperatures which separate the regions over which the dominant positive ions occur have also decreased as shown in Table 2. The largest concentrations of electrons and O⁻ ions (at T_g = 15000 K) have now decreased from 2×10¹⁷ cm⁻³ and 3 × 10¹¹ cm⁻³ respectively at p = 760 Torr as shown in reference [1], to less than 5×10¹⁴ cm⁻³ and 3×10⁹ cm⁻³ respectively at p = 10 Torr as shown in figure 3.

The results of the chemical kinetic model for positive ions have also been compared to the concentrations of Ar⁺, C⁺, and O⁺ ions predicted by the Saha equation [1–3], in figure 2. As shown in this figure, the the ion densities calculated by the

Saha equation for C^+ , Ar^+ , and O^+ are completely different from those calculated by the present chemical kinetic model. The Saha equation predicted ion densities not only overestimate the absolute densities but also the gas temperature dependencies due to the fact that the Saha equation does not account for ion-molecule reactions and the existence of the molecular ion generation and loss processes.

4 Analysis and Conclusions

An overall assessment of the changes brought on by the changes of the system pressure indicates that the gross features of the temperature dependencies of the ionized and neutral species have been conserved, but the relative concentration of species such as CO_2 and CO increase with increasing pressure as shown. The combined effects of the decreased importance of diffusion losses with increasing pressure, and the increase of the importance of three-body reactions in favour of two-body reactions due to the increased species densities brought on by the increase in the system pressure may be important contributing factors to this trend. The plasma density also increases with increasing pressure, but the change in the relative concentration of electrons with pressure can only be examined properly via the degree of ionization. A summary of the effects of pressure on the degree of ionization has been assembled in figure 5 for pressures between 10 Torr and 760 Torr, where the degree of ionization is defined as $\alpha = \frac{[e]}{N_{TOT}}$, where $[e]$ represents the concentration of electrons, and N_{TOT} represents the total concentration of atoms and molecules in the system. As indicated in figure 5, the degree of ionization tends to decrease with increasing pressure at temperatures greater than $T_g = 4500$ K. The largest degree of ionization $\alpha \approx 7 \times 10^{-2}$ occurs at $T_g = 15000$ K when $p = 10$ Torr. At temperatures greater than $T_g = 4500$ K, the electron concentration is determined primarily by the concentrations of O_2^+ , O^+ , and C^+ ions. Thus, although the absolute concentration of these species increases with increasing pressure as shown in figure 4, the concentration relative to the total concentration actually decreases. This effect may be due to a relative reduction in the concentration of the species in the reactions which act as major sources of O_2^+ , O^+ , and C^+ due to an increase in the relative concentration of such species as CO_2 and CO .

At temperatures less than $T_g = 4500$ K however, the degree of ionization tends to have a non-monotonic dependence on pressure, increasing with increases in pressure from $p = 10$ Torr to $p = 100$ Torr, remaining relatively constant between $p = 100$ Torr and $p = 760$ Torr, and decreasing at pressures greater than $p = 760$ Torr. The behaviour of the degree of ionization at these low temperatures is determined primarily by the concentration of the CO_4^+ ion.

Acknowledgements

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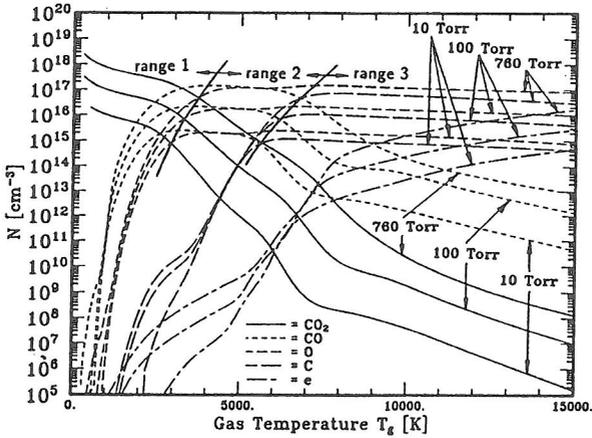


Figure 4: Summary of the effect of changing pressure on the temperature dependent concentrations of CO₂, CO, C, O, and electrons for an Ar-10%CO₂ mixture plasma.

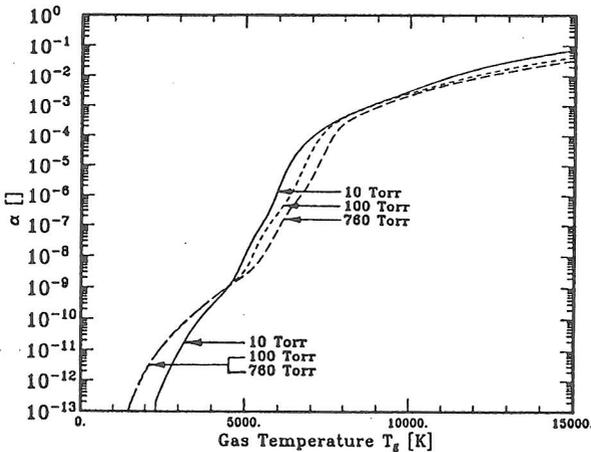


Figure 5: Summary of the effect of changing pressure on the degree of ionization for an Ar-10%CO₂ mixture plasma.