Conductivity Measurements of Phosphorus-Doped Potassium-Seeded MHD Plasmas

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The depression of electrical conductivity from the addition of phosphorus was measured for a potassium-seeded combustion product plasma at a temperature of ~1700 K and for three values of flame stoichiometry. A chemical equilibrium code was used to determine the values of the thermochemical constants of the phosphorus/potassium system that were in best agreement with all of the data. Tight constraints are placed on the thermochemical constants by the strong sensitivity of the predicted conductivity levels to the thermochemical constants used, especially when variations in conductivity levels with flame stoichiometry are considered. Equilibrium calculations based on these thermochemical constants confirm that, at the level of phosphorus expected in MHD generators (≤ 30 ppm), the effect of phosphorus should be minor (≤ 3-5% conductivity depression at 1800 K and less at higher temperatures).

Introduction

THE effect of ash-derived phosphorus impurities on coal-fired MHD generator systems has been a subject of debate and conjecture for several years.[1] Computations using the best available thermodynamic data at the time indicated the possibility of a substantial decrease in plasma conductivity due to the electron attachment to PO_2 and PO_3.[2] Prompted by these calculations, Annen et al.[3] conducted experiments that established an upper limit of a 15% decrease in conductivity under typical phosphorus loading (30 ppm). In the analysis of their data, only one phosphorus negative ion, PO_2^-, and no potassium phosphate salts were considered. More careful consideration of the phosphorus chemistry[4-6] indicated that the situation is more complex and that, while the effect of phosphorus is probably not great at typical loading levels, a greater understanding of the chemistry involved is of interest. In addition, it is useful to obtain additional data at lower temperatures (such as those expected in the boundary layer, rather than in the core) and to establish trends as a function of temperature and stoichiometry.

The chemistry of phosphorus also has importance in other fields. Hastie and Bonnell[6] have extensively studied the efficiency of phosphorus species as flame inhibitors and have indicated that phosphorus-based systems may provide a suitable replacement for halocarbons. In aqueous solution, PO_3^- has been postulated as an intermediate in phosphorylation reactions.[7] There are no thermodynamic data available in the literature for this species in either the gas or solution phase.

This paper describes experiments and supporting calculations that were performed to determine the thermodynamic data relevant to phosphorus chemistry. The thermodynamic data are provided indirectly by measuring the effect of phosphorus on plasma conductivity as a function of stoichiometry. The equilibrium chemistry of the phosphorus combustion system is such that the variation of conductivity with stoichiometry is quite sensitive to the thermodynamic constants.

Experimental Apparatus and Procedures

The experiments consisted of measurements of the depression of electrical conductivity of potassium-seeded combustion products flow by the addition of phosphorus. A small-scale burner was used to establish steady conditions and a simple probe used to measure the electrical conductivity. At constant burner conditions, the conductivity was first measured for pure potassium seeding, then for phosphorus-doped potassium, and finally for a repeat of the pure potassium conditions. In this way, relative conductivity measurements, less sensitive to experimental error, were obtained.

Burner

The laboratory burner[4] (see Fig. 1) used in this study was designed to burn mixtures of methane, air, and oxygen with provisions for adding gaseous or particulate seeds. The burner has been operated over a wide range of stoichiometry ($0.8 \leq \phi \leq 1.2$, $\phi \equiv$ equivalence ratio) and with oxygen content up to 40% oxygen by volume. The combustion gases are metered and premixed prior to injection through 1 mm i.d. stainless steel tubes in the 0.10 m diam back plate of the burner. Flowmeter tubes (Matheson) were individually calibrated and could be set to within an accuracy of 5%. The 0.70 m long burner duct provides sufficient residence time to insure equilibrium even at the highest mass flows used in the facility. An average residence time of ~0.3 s is obtained at a flow of 150 liter/min (0.003 kg/s). A well-insulated ceramic wall maintains relatively isothermal conditions in the burner duct despite the long residence time. Thermocouples were used to measure the plasma temperature at several locations down the channel; early experimental measurements established a gas temperature drop of $\lesssim 150$ K and an outlet temperature of ~1800 K for nominal conditions. Further details of the system construction and operation are reported in Ref. 8.

Seed Injection System

The seed material was injected as an air-fluidized flow of particles with a mean diameter of less than 100 μm. A Plasmadyne Rotor-feeder was supplied with air at a known flow rate and used to feed the material through a port in the burner duct 0.2 m downstream of the burner end plate. This location was preferred over injection into the main oxidizer flow because it reduced the number of locations where seed material of one phosphorus level could accumulate and possibly be injected during testing with seed material of

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another phosphorus concentration. For similar reasons, the fluidizer was disassembled and thoroughly cleaned each time the seed mixture was changed. Mixtures of pulverized potassium carbonate (K_2CO_3) and potassium phosphate (KH_2PO_4) were prepared prior to the tests and were kept dry in an oven at 400 K.

Conductivity Probe Measurements

The combustion products flow down the burner duct, are accelerated to a speed of ≤ 50 m/s in a ceramic nozzle, and then passed into the conductivity measurement probe. The probe is constructed from magnesia ceramic and has a thermocouple installed in the ceramic near the entrance and thermocouples inserted into the flow at the inlet and exit of the probe. The probe, shown in Fig. 2, uses the standard "four-pin" probe technique[9,10] to measure the average conductivity without interference from electrode voltage drops. The voltage probes and electrodes are constructed of 0.5 mm diam platinum wire. Voltage is applied to the outermost electrodes and the conductivity determined from the measured current and the measured intermediate electric field. The distance between the probes and the electrodes is chosen large enough to allow the current to spread and fill the circular flow area; this reduces the indirect effects of the small electrode area and of the flow phenomena induced by the electrode that stretches across the passage. The result is a measure of conductivity averaged over the flow cross section and over the axial length separating the probes by which the electric field is measured.

Evaluation of the absolute conductivity level with great accuracy is difficult because of the rather pronounced temperature drop from the centerline to the wall in the probe and an axial temperature gradient. Nonetheless, calculations made assuming a reasonable temperature profile in the cross section show that measurements of the conductivity ratio for two phosphorus loadings at fixed combustor conditions can be accurately interpreted. Leakage of current through the probe and through seed deposits on the probe surface can also cause errors for the relatively low conductivities of these experiments. These leakage currents were determined by measuring the current with the flow through the probe momentarily interrupted by blocking the end. Two other sources of error were residual seed in the system and fluctuations, primarily from variations in the fluidized seed flow.

Experimental Results

For all of the reported results, the total burner flow rate was 150 liter/min. The stoichiometric ratio was varied from 0.90 (fuel lean) to 1.14 (fuel rich); oxygen enrichments of 0.30 and 0.35 by volume were run. The temperature of the gas in the probe was 1660-1800 K. The potassium seed flow rate was set at approximately 0.63% by weight and the phosphorus fraction chosen to give a depression of approximately a factor of 2; note that this phosphorus loading corresponds to 240 ppm, compared to the expected level of <30 ppm in an MHD generator. An increase in phosphorus concentration by a factor of 5 lowered the conductivity to a level below the leakage, while a decrease by a factor of 10 results in a depression too small to measure with accuracy.

The results are summarized in Table 1, where the ratio of plasma conductivity with and without phosphorus, σ/σ_0, is shown. The measured gas temperature at the probe inlet and the combustor conditions are also shown. The absolute conductivity inferred from the data for pure potassium is in the range of 0.01 to 0.03 mho/m, which is consistent with the measured temperature; the uncertainty in this measurement is high but the agreement is still encouraging. The large error in the measured conductivity ratio is partly from fluctuations in the seed flow rate and partly from leakage through the seed layers on the probe.

The important result is that the conductivity ratio was constant over the temperature and stoichiometry ranges for which the experiments were performed. Even with the large uncertainty, this result has strong implications for establishing accurate thermodynamics data for the potassium/phosphorus system. The next section discusses the interpretation of the presently measured results and the results of Annen et al.[3]

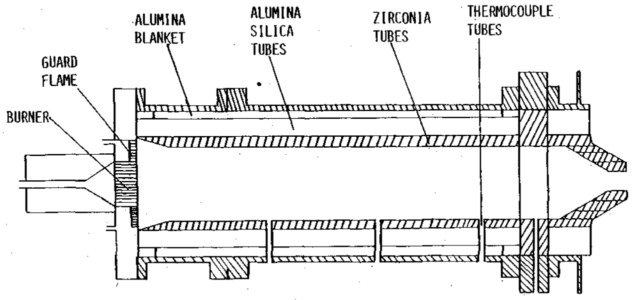

Fig. 1 Laboratory scale burner and insulated channel.

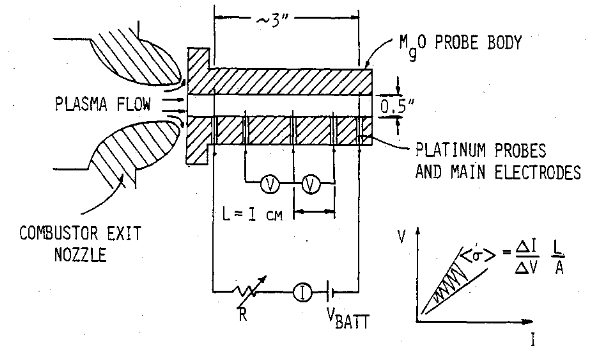

Fig. 2 Sketch of conductivity probe showing the applied voltage circuit [relatively high voltage levels (~50-200 V) are applied].

Table 1 Conditions and results of present investigation

ϕ	$\frac{O_2}{O_2+N_2}$	T, K	Mole fraction		Measured σ/σ_0	Calculated σ/σ_0		
							ΔH_f (KPO_2), 6 kcal/mole	
			Potassium	Phosphorus		"Best"	(More stable)	(Less stable)
0.90	0.30	1700±40	4.5×10^{-3}	2.4×10^{-4}	0.61±0.20	0.51	0.53	0.51
	0.35	1730			0.65	0.50	0.52	0.51
0.94	0.30	1720			0.61	0.51	0.54	0.51
1.10	0.30	1660			0.56			
	0.30	1660			0.75	0.54	0.80	0.32
	0.30	1720			0.59			
	0.25	1720			0.66	0.52	0.80	0.33
1.14	0.30	1800			0.55	0.57	0.83	0.32

Interpretation of Results

Under the conditions used in the present experiment and current MHD generators, the chemistry involved in the potassium/phosphorus system can be approximated by the following equations:

$$K \rightleftharpoons K^+ + e^- \tag{1}$$

$$KPO_2 + e^- \rightleftharpoons K + PO_2^- \tag{2}$$

$$KPO_3 + e^- \rightleftharpoons K + PO_3^- \tag{3}$$

Essentially, all of the phosphorus is bound into the alkali salts (KPO_2 and KPO_3) with the phosphorus negative ion concentrations being two to four orders of magnitude lower than the neutral salts. However, since the free-electron concentrations can be of the same order of magnitude as those of the anions, relatively small uncertainties in the heats of formation of the above species can cause large uncertainties in calculating the conductivity. The thermodynamic constants required to determine the effect of phosphorus are the heats of formation of KPO_2 and KPO_3 and the electron affinities of PO_2 and PO_3. Fortunately, the electron affinity of PO_2 has recently been measured with good reliability by Wu and Tiernan[11] to be 3.3 ± 0.1 eV, which provides a cornerstone for the determination of other values.

The efficacy of this experiment in determining thermodynamic functions is based on the fact that Eqs. (2) and (3) are strong functions of stoichiometry. LeChatelier's principle favors formation of KPO_2 and PO_2^- under fuel-rich conditions, while oxygen-rich conditions favor KPO_3 and PO_3^-. The constancy of the plasma conductivity depression caused by phosphorus points to the chemical buffering effect of Eqs. (2) and (3) and places great constraints on the flexibility in choosing thermodynamic values for the above species. Further data, shown in Table 2, are provided in Annen et al.[3] under similar conditions but at temperatures of 2275 and 2380 K. In these experiments, absolute free-electron concentrations were measured with a submillimeter laser system, thus providing a stringent test for any modeling efforts.

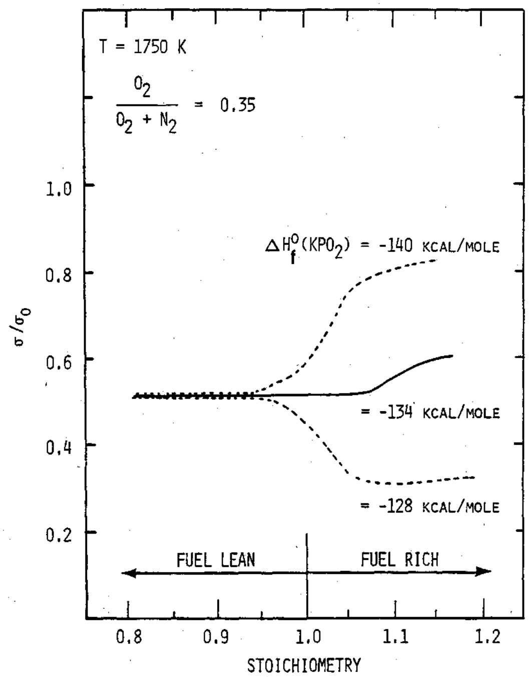

Fig. 3 Calculations of the ratio of potassium-seeded plasma conductivities with and without phosphorus addition as a function of stoichiometry for various heats of formation of KPO_2 (potassium loading is 0.63% by weight and the phosphorus level is set at 240 ppm). Note that varying the thermodynamic parameters for KPO_2 has an effect only under fuel-rich conditions.

Modeling calculations were performed with an equilibrium thermochemistry code (PACKAGE)[12] developed with particular attention to the influence that nonfuel coal components, such as inorganic oxides arising from ash oxidation and vaporization, may have on plasma composition and conductivity. The free-energy minimization routine used in this code is based on the NASA chemical equilibrium code (CEC).[13] Plasma conductivity is calculated using an algorithm developed by Demetriades and Argyropoulos.[14] Values for the heats of formation determined by the trial-and-error fitting of the present data and the data of Annen are

$$H_f^0 \; (KPO_2) = -134 \pm 6 \text{ kcal/mole}$$

$$H_f^0 \; (KPO_3) = -189 \pm 6 \text{ kcal/mole}$$

$$H_f^0 \; (PO_3^-) = -190 \pm 6 \text{ kcal/mole}$$

The uncertainties represent the relative changes in the heats of formation needed to cause a poor fit to the data using a fixed value for ΔH_f^0 (PO_2^-). Uncertainties in the absolute scaling of the whole set of heats of formation are ±3 kcal/mole; this reflects both ignorance of the structural properties of these molecules and the uncertainty in the PO_2 electron affinity. The sensitivity of the thermodynamic constants to the data is shown in the last two columns of Table 1 and in Fig. 3, which plots the conductivity depression as a function of stoichiometry for three values of the heat of formation of KPO_2. When ΔH_f^0 (KPO_2) is made more or less stable by 6 kcal/mole, the calculated conductivity reduction is clearly outside the scatter of the present data under fuel-rich conditions; furthermore, the calculated electron concentration does not fit the data of Annen. Similar results are obtained for other variations in the heats of formation of KPO_3 and PO_3^- under fuel-lean conditions. The inferred electron affinity of 4.9 eV for PO_3 [assuming ΔH_f^0 (PO_3) = −78 kcal/mole), see Ref. 3] is within the range of a theoretical calculation of 4.4-5.3 eV.[15] Both the bond strength of KPO_2 and the relative stability of KPO_3 to KPO_2 are in agreement with the work of Gingerich and Miller[16] who measured the heats of formation of the sodium phosphate salts.

Summary and Conclusions

The depression of electrical conductivity by the addition of phosphorus was measured for a combustion products plasma at temperatures of ~1700 K. The ratio of conductivity with and without 240 ppm of phosphorus was 0.60 ±0.20 independent of the stoichiometric ratio that was varied from 0.90 to 1.14 (fuel rich). Equilibrium calculations based on the thermochemistry established in these experiments confirm that, for the phosphorus levels of ≤30 ppm expected in MHD generators, the effect of phosphorus should be to decrease the

Table 2 Conditions and experimental results of Annen et al.[3] and results of present calculations

			Mole fraction			Calculated n_e^-, m^{-3}		
							ΔH_f (KPO_2), 6 kcal/mole	
ϕ	$\frac{O_2}{O_2+N_2}$	T, K	Potassium	Phosphorus	n_e^-, m^{-3}	"Best"	(More stable)	(Less stable)
0.9	0.42	2275	7.0×10^{-3}	3.1×10^{-4}	$8.2 \pm 2.0 \times 10^{18}$	10.1×10^{18}	11.7×10^{18}	9.2×10^{18}
0.9	0.51	2380	8.4×10^{-3}	3.7×10^{-4}	$2.2 \pm 2.0 \times 10^{19}$	2.1×10^{19}	3.4×10^{19}	1.9×10^{19}

conductivity by no more than 3-5% at temperature of 1800-2000 K and by less at higher temperatures.

The measured conductivity data and the measured electron number density data of Annen were used to determine the thermodynamic constants relevant to the potassium/phosphorus system. The calculated variation of conductivity depression from the phosphorus depends strongly on the thermodynamic data, so that the measured data place tight constraints on the thermodynamic constants. Assuming the recently measured electron affinity for PO_2 (implying ΔH_f^0 $(PO_2^-) = -138$ kcal/mole), the following values were determined:

$$\Delta H_f^0\ (KPO_2) = -134 \pm 8\ \text{kcal/mole}$$

$$\Delta H_f^0\ (KPO_3) = -189 \pm 8\ \text{kcal/mole}$$

$$\Delta H_f^0\ (PO_3^-) = -190 \pm 8\ \text{kcal/mole}$$

The experience with phosphorus species shows the need for care in the planning and interpretation of measurements and in the application of chemical equilibrium codes to calculate the effects of trace species whose thermodynamics are not well understood. These measurements also underscore the usefulness of small laboratory-scale burners in determining plasma properties (such as conductivity).

Acknowledgments

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