PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
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Composition and Thermodynamic Properties of Combustion Products of Methane Containing Potassium Carbonate

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XII. Composition and thermodynamic properties of combustion products of methane containing potassium carbonate

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The paper describes calculations and some computations of the composition of combustion products of methane and oxygen-enriched air between 1000 and 4000 °K. The effect of introducing potassium into the mixture is considered. This gives rise to the presence of electrons in large quantities and to certain redistributions in the proportions of some compounds and, at different temperatures, to the formation of a variety of potassium compounds. The formation of those compounds has a considerable effect on the concentration of electrons.

1. Introduction

There are several uncertain factors which must be resolved before m.h.d. generation becomes anything more than a promising development. One aspect which has been investigated already in some detail is the prediction of the electrical and thermodynamic properties of the plasma obtained by burning in air fuels with additions of ionizable seed. Most of the available data is for oils and coals (Moffat 1962; Frost 1961; Mori *et al.* 1965) in which the carbon: hydrogen ratio of the fuel is about 1:2. This paper considers the products of combustion of methane in air with and without the addition of potassium carbonate.

2. Calculations and results

The calculation of the equilibrium composition of the plasma requires the solution of a system of non-linear equations. These include equations involving equilibrium constants to describe chemical equilibrium and equations to satisfy the total pressure condition, electrical neutrality and conservation of species. The equations have been solved on a BESM-2 computer by means of a program written by Rtishcheva & Vorobyov. The molecular weight, enthalpy, entropy, specific volume and composition of the plasma were computed. The zero of enthalpy was taken as the standard states of the elements at 0 °K, i.e. C (graphite), O_2, H_2, N_2, Ar (gases) and K (crystal).

Basic data of equilibrium constants, specific heats, heats of formation and entropy of the plasma components were obtained from Gurvich *et al.* (1962) except for data on KO, KH, KOH and $(KOH)_2$ which were obtained from the JANAF tables. About sixty different molecular and atomic species were considered in the calculations.

The elemental proportions of C, H, N, O used in the calculations were determined by the conditions of burning CH_4 in air of normal composition (20·95 % O_2, 78·08 % N_2 and 0·97 % Ar) (Predvoditelev *et al.* 1957); also in air enriched with oxygen up to 30 % O_2 and 40 % O_2 and in air enriched with nitrogen to give 81·08 % N_2 and with fuel to air ratios of 0·9, 1 and 1·1. The nitrogen enriched air composition may be considered as an approximation to burning natural gas (which usually contains a certain percentage of nitrogen as well as methane) in air.

The quantity of K_2CO_3 added as seed corresponded to 1% of potassium content in the mixture. (All the concentrations are given as percentages by volume.) When calculating the elemental composition of the mixtures containing K_2CO_3, the total quantity of carbon and oxygen also included the content of these elements in the potassium carbonate.

Calculations were made at temperatures from 1000 to 4000 °K at 200 degK intervals and at 17 pressures from 0·2 to 100 atm. Figure 1 shows a typical Mollier chart for one case with and without seed. Figure 2 (*a*) shows how the partial pressures of the components vary with temperature without seed and figure 2 (*b*) shows the same thing with seed present.

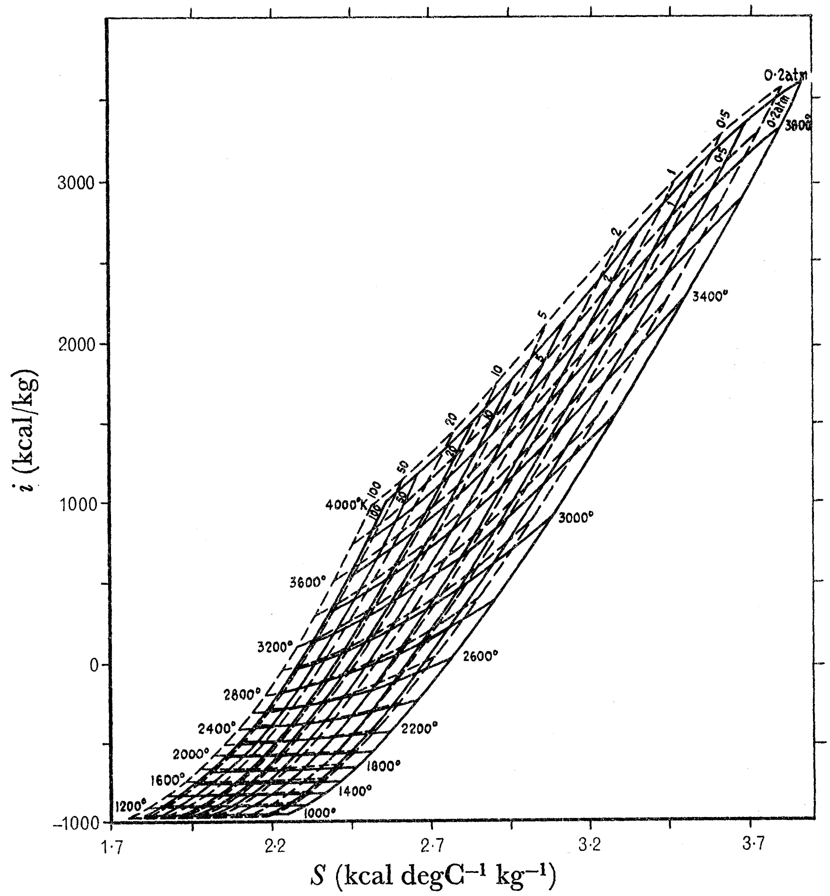

FIGURE 1. Mollier chart for the stoichiometric products of methane in air; CH_4 + (20·95 % O_2 + 78·08 % N_2 + 0·97 % Ar). The full lines refer to unseeded gases, the dashed lines to gases with K_2CO_3 added to give 1 % K in the gases.

DISCUSSION

First, it is worth pointing out that the calculations described here take into account some components not considered by other authors (Moffatt 1962; Frost 1961; Mori *et al.* 1965) and that some of these may have quite high concentrations. For example HO_2, NH, HNO, HCO, NO_2 and N_2O amongst neutral species and O^-, H^-, OH^- among charged species. Under certain conditions these 'high-temperature' components become very important and their consideration can greatly add to the accuracy of equilibrium composition calculations. The presence of negative ions in particular may reduce the electrical conductivity of the gas.

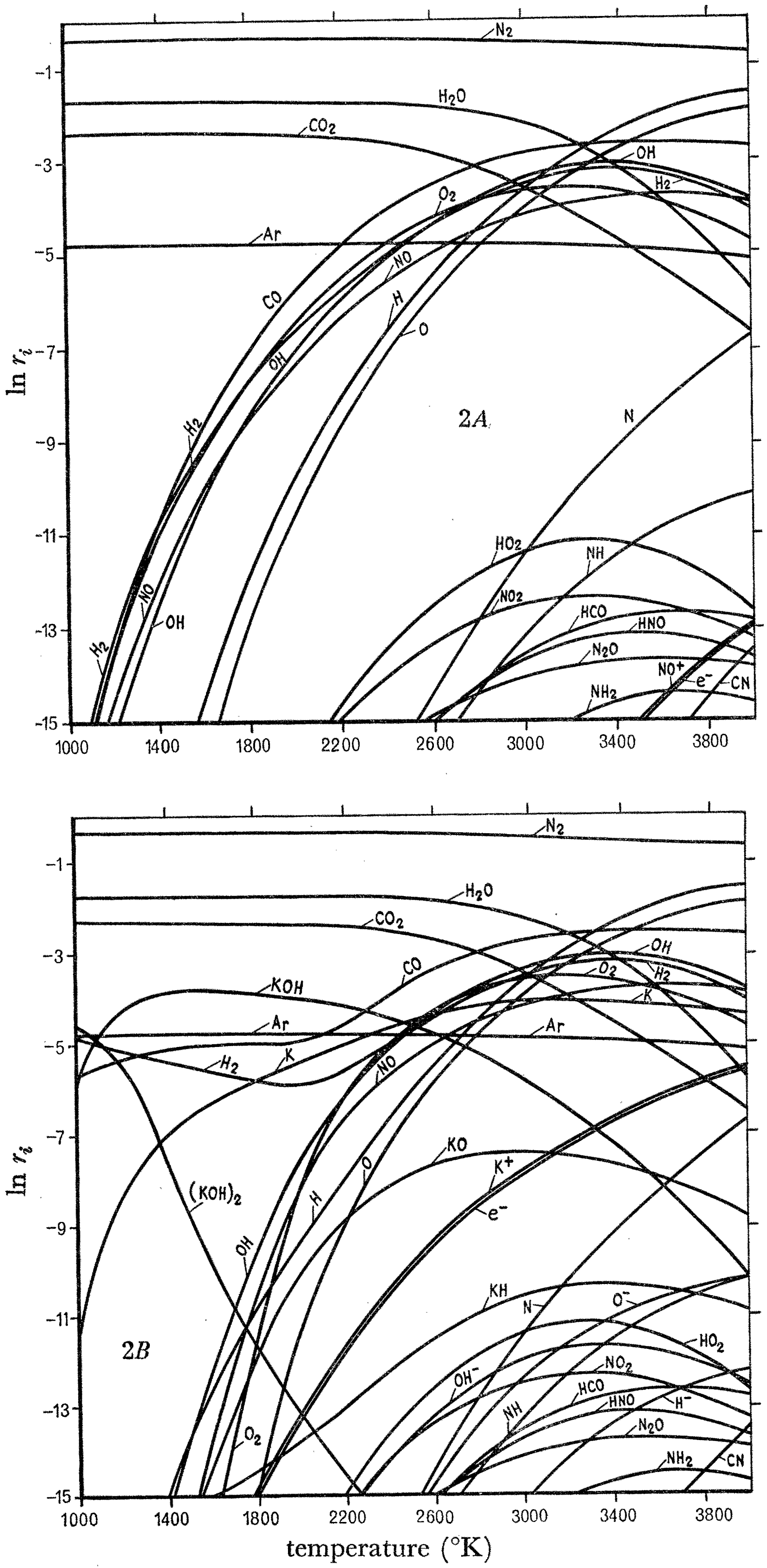

FIGURE 2. Variation with temperature of partial pressures, r_i, of constituent species in combustion products of methane and air. (*a*) Refers to unseeded gases and (*b*) to gases seeded with K_2CO_3 to give 1 % K in the gas. The natural logarithm pressure is shown; the total pressure is 1 atm.

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The second special aspect of these calculations is the consideration of potassium compounds (KO, KH, KOH, $(KOH)_2$) which Moffatt and Frost ignored. The formation of such compounds reduces the concentration of potassium atoms and consequently of ionized potassium and electrons so that those earlier calculations may be expected to have overestimated the electrical conductivity. These considerations refer mainly to the fairly low temperature region where the potassium molecular compounds are still fairly stable.

In addition to the compounds considered in the present calculations there are at least two others for which data have appeared in recent years tending to suggest the possibility of their existence in the gaseous state. These are K_2O and K_2CO_3. However, estimates based on the results of mass spectrometric analysis of K—O and K—O—C systems (carried out by A. V. Gusarov and L. N. Gorokhov at the High Temperature Institute and Moscow State University) showed that under the conditions considered in this work neither of these compounds is formed in any appreciable quantity.

Finally, the chemical composition of the gases is strongly influenced by the addition of potassium carbonate. Below 2000 °K the O_2 content is reduced and the CO content increased. A shallow maximum in H_2O concentration and an anomalous minimum in H_2 concentration occur at about 2000 °K. All these features are clearly caused by the formation of potassium compounds and mostly by the formation of KOH which largely dissociates above 2000 °K when the effects on chemical composition of adding K_2CO_3 become less pronounced though still noticeable.

The calculations of the quantities of potassium compounds formed and of their effects are based on rather uncertain data. A study of errors in heats of formation of the two major compounds KO (± 15 kcal/mole) and KOH (± 5 kcal/mole) shows considerable effect on their partial pressures but for all practical purposes no effect on either the electron concentration or the thermodynamic properties of the plasma.

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