AIP Journal of Applied Physics

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Citation: Journal of Applied Physics **50**, 3935 (1979); doi: 10.1063/1.326417
View online: http://dx.doi.org/10.1063/1.326417
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/50/6?ver=pdfcov
Published by the AIP Publishing

Hydrogen-isotope separation in dc-arc plasma[a)]

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(Received 16 October 1978; accepted for publication 16 February 1979)

In an arc plasma (230 A) burning in an atmosphere of air and argon a vapor-probe mixture of D_2O and H_2O was introduced. Samples were taken with a Calprobe water-cooled probe from the plasma gas at the same axial position in the arc column, but at different radial distances. The results of mass-spectrometric analyses are presented in two groups: for the samples taken from arc regions having temperatures above 5900 K and for those taken below 3800 K. An isotope separation factor is found between these regions of higher and lower temperature: (D:H) (high temp.):(D:H) (low temp.) $= 1.67 \pm 12\%$.

PACS numbers: 52.80.Mg, 31.30.Gs

I. INTRODUCTION

The radial distribution of particles of different elements in a dc arc plasma cannot be described without taking into account the radial mass-separation effect.[1–10] With a low-current arc (10 A) it was found that this effect depends on the degree of ionization of the elements.[11–12] With a low-current arc, investigations were also made with hydrogen isotopes in the following way.[13]

The arc was burning in air; the lower electrode was an anode. A mixture of D_2O and H_2O (approximately 1 : 1) was fed to the anode. The water evaporated during arc burning. Because of the presence of water vapor, the arc characteristics were considerably changed.[14–16] The radial distributions of emission for D_α and H_α lines were determined spectroscopically. The results showed that when both radial distributions were normalized to the intensity of H_α in the central part of the plasma, the curve for D_α was higher than for H_α. The results are described by the factor f_1:

$$f_1 = \frac{{}^iD_\alpha : {}^iH_\alpha}{c_{D_2O} : c_{H_2O}},$$

where $({}^iD_\alpha : {}^iH_\alpha)$ is the ratio of the intensities of the spectral lines D_α and H_α, and $(c_{D_2O} : c_{H_2O})$ is the ratio of concentrations of D_2O to H_2O in the water.

It can be assumed that the ratio ${}^iD_\alpha : {}^iH_\alpha$ corresponds to that of the particles' densities D : H. Further, it can be assumed that the ratio of D : H in the water is not considerably changed in the water vapor surrounding the arc plasma.

A diffusion of the molecules D_2O, HDO, and H_2O occurs from peripheral zones into central arc zones of high temperature. Molecules and radicals dissociate and atoms diffuse in opposite direction to the colder zones. The isotopic difference in diffusion velocities of the molecules D_2O and H_2O, based on mass differences, is much smaller than the difference in the diffusion velocities of H and D.

This might be one of the causes of the observed effect. From this point of view, the temperature of about 4000 K (where most of the water molecules dissociate) is significant. Therefore, the high-temperature zone in the arc plasma can be regarded as the high temperature between 4000 K and the temperature in the arc axis (about 9000 K in the observed case); the low temperature zone is from 4000 K to room temperature.

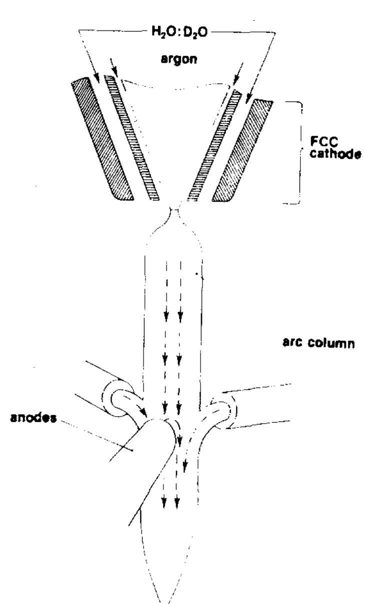

FIG. 1. Scheme of dc arc with fluid-convention cathode and three anodes.

[a)]This paper was presented in part at the Gordon Conference on Plasma Chemistry, Andover, N.H., 1978.

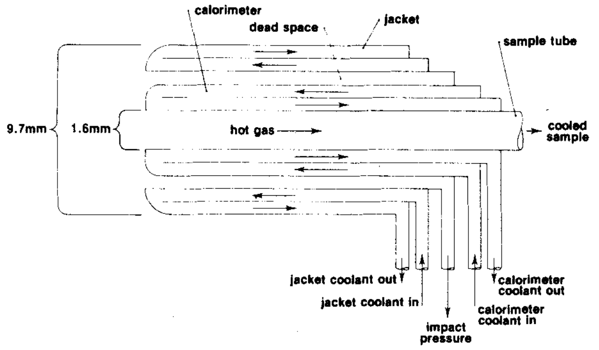

FIG. 2. Scheme of Calprobe nozzle.

In Ref. 13, the radial distribution of the factor f_1 is given (the measurements involve only the plasma temperature zones considerably higher than 4000 K). The radial distribution of f_1 was almost constant at about 1.5.

Reference 13 described the spectroscopic measurements during the arc burning. Although these investigations showed the existence of the hydrogen-isotope separation effect in the arc plasma, the questions remained as to how the gas from the different temperature zones could be separated and how to achieve an isotope separation when the arc is switched off. It was necessary to take samples of the gas plasma above and below 4000 K.

II. EXPERIMENT AND DISCUSSION

The high-current arc (230 A) with a fluid-convection cathode and three anodes was used. This type of arc was developed by Sheer, Korman, and Kang.[17] The schematic view of the arc is given in Fig. 1.

The tip of the cathode was made of tungsten, the other parts of copper. The anodes were made of copper tubes, surrounding at the end a piece of porous graphite. An intensive flow of hot water circulated through the cathode and the anodes. Argon was introduced through all electrodes. A vapor mixture of D_2O and H_2O was introduced through the cathode. The steam was produced by a small generator. The arc was burning mainly in an atmosphere of air (open arc) and argon.

For sampling the gas plasma, the Calprobe, a water-cooled aspirating calorimeter probe (made by the Calprobe Corp.) was used. Figure 2 explains the main operating features of the Calprobe. Through two concentric tubes (in the cross-sectional form of a ring) water circulates under pressure from a water pump. The inner tube is a calorimeter with the outer a jacket protecting it. The hot gas is sucked through the axial passage of the probe. During the flow through the probe, gas gives heat to the calorimeter. By measuring the increase in temperature of the water circulating through the calorimeter, it is possible during sampling to obtain information about the enthalpy of the gas. Gas enthalpy is equal to the increase in the enthalpy of the inner coolant, plus some residual enthalpy after cooling at the probe exit. The total enthalpy can be expressed as

$$h_{g1} + \frac{\dot{m}_c Cp_c \Delta T_c}{\dot{m}_g} + Cp_{g2} T_{G2}. \tag{1}$$

From the enthalpy measurement, it is in some cases also possible to obtain information about the gas temperature:

$$T_{g1} = \frac{\dot{m}_c Cp_c \Delta T_c}{\dot{m}_g Cp_{g1}} + \frac{Cp_{g2} T_{g2}}{Cp_{g1}}. \tag{2}$$

In these expressions h_{g1} is the total enthalpy of the gas to be measured, T_{g1} is the total temperature of gas to be measured, ΔT_c is the coolant temperature rise (measured by thermocouples incorporated into the probe), T_{g2} is the gas-sample exit temperature (measured by thermocouples incorporated into the probe), $\dot{m}_c$ is the coolant flow rate, $\dot{m}_g$ is the mass flow rate of the gas sample, Cp_{g2} is the mean heat capacity of the gas sample at temperature T_{g2}, Cp_{g1} is the mean heat capacity of the gas sample at gas temperature T_{g1}, and Cp_c is the mean heat capacity of the calorimeter coolant.

In many cases, it is possible to neglect the second member in expression (1) and (2). The Calprobe was introduced into the arc normal to the column at a distance of 12 mm below the anodes. The samples were taken at the same horizontal level, but at different radial distances. Simultaneously, an increase in temperature ΔT_c of the water circulating through the calorimeter was recorded.

Analyses of the samples were made by mass spectrometer. On the basis of these results, taking into account the main components of the gas (N_2, O_2, Ar, and NO) the mean heat capacity of each sample at different temperatures was calculated. For these calculations, the data on gas heat capacities from Burnhorn and Wienecke[18] and Drellishak, Knapp, and Cambel[19] were used.

In this way, using Eq. (2), the dependence of the difference of temperature ΔT_c of the coolant circulating through the calorimeter from the gas temperature T_{g1} was obtained for each sample. The curves of ΔT_c as a function of T_{g1} often show maxima. Such maxima are connected with the influence of chemical reactions on gas heat conductivity. In this case, the maxima were about 4000 and 7000 K; this is connected with the dissociation of O_2 and N_2. There is an uncertainty in the determination of temperature T_{g1} when one ΔT_c value measured could relate to both sides of a curve around the maxima. In cases when such uncertainty existed, i.e., when samples could be related to gas-temperature region both above and below 4000 K, the results of these samples were not taken into account.

The results are presented in two groups, namely, for samples taken from the "high" and the "low" temperature regions, respectively. High temperature here means between 5900 and 6700 K; low temperature means between 3000 and 3800 K.

During the arc burning, samples were taken alternately from each region.

The mean values for the volume percentage of D_2, HD, and H_2 from seven measurements related to the high-temperature region and five to the low-temperature region are given in the histogram in Fig. 3.

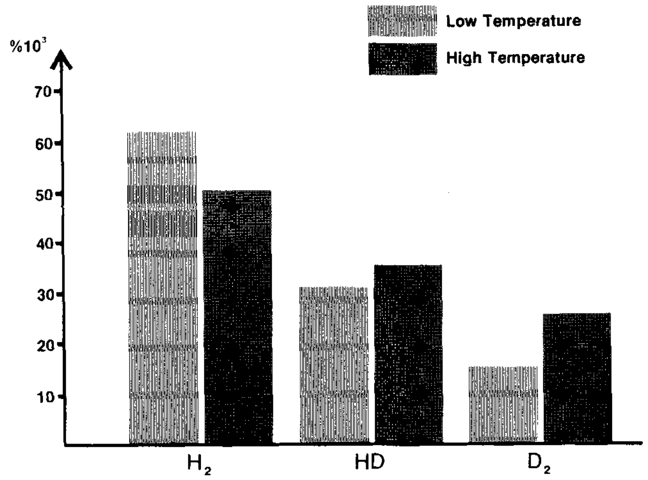

FIG. 3. Mean values of volume percentage for D_2, HD, and H_2 for samples taken at high- and low-temperature regions.

For every sample, the ratio (D :H) of atoms was calculated. In these calculations, the values for HD were included. The quotient between the mean value of these relations for samples from high- and low-temperature regions can be observed as the isotope separation factor f_2 between these two temperature regions in the plasma.

It is found that

$$f_2 = \frac{\text{D : H(hightemp.)}}{\text{D : H(low temp.)}} = 1.67\% \pm 12\%$$

The error was calculated on the basis of the standard errors of the mean value (D : H) for each region.

This result shows that it is possible to take samples from different radial plasma zones and obtain hydrogen-isotope separation in a dc-arc plasma.

How efficient the sampling is from different plasma zones, especially because of the processes in the gas layer on the surface of the probe, has not yet been resolved. The result obtained for f_2 is in agreement with previous spectroscopic measurements made with a low-current arc.

It might be proposed that the mechanism of the effect is connected with the mass transport in the plasma. One of the possible explanations might be, as has been described before, the difference of transport of D and H atoms.

When the plasma is surrounded by water vapor, two opposite radial diffusion streams have to be taken into account: one is the diffusion of molecular components from the periphery of the plasma to the central zones where dissociation occurs, the other is the diffusion of atomic components from the zones of higher temperature to the periphery. For the molecular components when binding with oxygen (as occurs with nitrogen) the isotopic differences in mass (H_2O, HDO, D_2O, OH, and OD) are relatively small. Accordingly, there should be no essential difference in the diffusion velocity in the direction from the peripheral zones to the central ones, but there should exist a difference in the transport in the opposite direction because of the mass difference of D and H.

As expected, the results for the measured diffusion coefficients in the arc plasma given in REfs. 20–23 show the dependence on the mass of the particles.

The differences in the rate constants of gas reactions between hydrogen isotopes are mentioned in many papers in the literature. It is now open as to how these differences may and can influence the effect described here.

One may draw the conclusion that isotopic separation of (D : H) is achieved in an arc plasma. The samples were taken from the central zone, where the hydrogen is largely present as atoms, and in the peripheral zone, where hydrogen is largely in molecular components.

ACKNOWLEDGMENTS

The authors wish to thank Dr. Charles Sheer and Dr. Samuel Korman of the Arc Research Laboratory, Dept. of Chemical Engineering Columbia University, who made these investigations possible in the Arc Research Laboratory and who were always ready to offer their assistance.

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