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Berkeley, California

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THE EFFECT OF OXYGEN, NITROGEN, AND WATER IN LOW-PRESSURE HYDROGEN DISCHARGES*

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One of the most persistent observations associated with the use of low-pressure electrical discharges for producing atoms from diatomic molecules has been that small quantities of impurities, such as water, greatly increase the atom yield. Wood,[1] Bichowsky and Copeland,[2] and Lord Rayleigh (R. J. Strutt)[3] were among the first to study the effect of such impurities in hydrogen, oxygen, and nitrogen discharges, respectively. Despite the efforts of a number of investigators, however, there still appears to be no agreement on the role of these gaseous impurities in the various molecular-gas discharge systems. The most recent papers tend only to confirm this viewpoint, as well as the fact that the entire problem is open for reinvestigation and clarification.[4-9] To help resolve this situation, studies were made of the role of oxygen, nitrogen, and water in increasing the yield of atomic hydrogen from a low-pressure hydrogen discharge.

The flow-tube system consisted of a mercury-plug flowmeter for H_2, a constant-volume bulb for O_2, N_2, or H_2O, a 150-cm long 37-mm i.d. Pyrex discharge and reaction tube, a Wrede-Harteck gauge, a thermocouple probe consisting of an iron-constantan thermocouple soldered to a 4-cm^2 piece of silver foil, a McLeod gauge, a diffusion pump for outgassing, liquid-nitrogen traps, and a large mechanical pump. Flow rates were about 0.08 cm^3/sec STP of H_2 at a system pressure of 75 to 85 mtorr.

A cyclotron-resonant microwave discharge maintained by a 100-W 2.45-GHz diathermy unit and cavities Nos. 2A (but larger in diameter) and 5 described by Fehsenfeld, Evenson, and Broida[10] was used, in addition to a 50- to 500-W 50 MHz electrodeless discharge, to produce the atomic hydrogen. The Wrede-Harteck gauge constructed in the Laboratory was capable of detecting 0.06% atoms at 75 mtorr.

The cylinder hydrogen, which eventually was shown to be very pure (99.99+%), was either used directly, passed through a water bubbler, or additionally purified with a hot silver-palladium alloy thimble. Oxygen and nitrogen were used directly from cylinders without further purification.

The results were: the addition of small amounts of oxygen to pure hydrogen stoichiometrically increased the yield of atoms from the low-pressure 50-MHz discharge by a ratio of at least two atoms per molecule of oxygen. Molecular nitrogen had a similar but smaller effect, which started to saturate at low concentrations of nitrogen. On the other hand, the addition of small amounts of water had no effect on the yield of atoms from the low-pressure discharge. The Wrede-Harteck gauge did not discriminate between atoms of hydrogen, oxygen, or nitrogen.

Since the observation concerning the effect of water conflicted with numerous previous results and disagreed with the current practice of bubbling hydrogen through water to increase atom yields, it was further tested in several different ways. However, the tests, cited below, only confirmed the original observation:

a. It was independent of the type of discharge used (microwave or 50 MHz) and the location or power level of the discharge;

b. It was independent of the source of hydrogen gas (directly from a cylinder or purified with the silver-palladium thimble);

c. It was independent of the source of water (distilled water added separately, distilled water in a water bubbler, or water formed from the closed volume or flow conversion of an oxygen-hydrogen reaction mixture);

d. It was independent of the atom-concentration measurement technique (two Wrede-Harteck gauges or a thermocouple probe);

e. It was independent of the initial surface properties of two different Pyrex reaction tubes and a quartz discharge tube;

f. The use of atomic nitrogen to clean the Pyrex walls had no effect on the results; and

g. The effects of oxygen and water were independent and superimposable when both were simultaneously added to the hydrogen gas.

These experiments led to the unmistakable conclusion that water, at least in the apparatus and under the experimental conditions cited above, did not influence the yield of atomic hydrogen from the low-pressure discharges.

The interesting question that now arises is: could this result be correct and generally applicable? A report (which also describes the above experiments in more detail) discusses several aspects of previous results on this phenomenon:[11]

a. Shaw's results partially confirm the present ones, even though his percent-dissociation values seem too high;[7]

b. The observation of high atom yields with hydrogen containing water does not prove that the water present is responsible;

c. The isothermal calorimeter may give "measured" atom-concentration values that are much higher than the actual ones; and

d. Since there are probably several different mechanisms for producing ground-state or excited-state atoms, the intensity of

the discharge color or the Balmer lines cannot be used as a reliable qualitative indication of the yield of atomic hydrogen from low-pressure discharges.

Thus, the above question cannot be settled from a consideration of the previous literature alone, but instead must be answered by independent investigations in (hopefully) the near future.

If the results obtained in these experiments with water are confirmed and shown to be generally applicable, some kinetic investigations with atomic hydrogen may have to be re-examined. These results may also have a bearing on current difficulties with the production of a continuous $H\text{-}Cl_2\text{-}HCl$[†] chemical laser maintained by a hydrogen discharge and a separate stream of chlorine gas.

FOOTNOTES AND REFERENCES

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