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THE DEVELOPMENT OF ULTRA-HIGH VACUUM TECHNIQUES FOR THE PURIFICATION OF NITROGEN GAS

by

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THE DEVELOPMENT OF ULTRA-HIGH VACUUM TECHNIQUES FOR THE PURIFICATION OF NITROGEN GAS

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Foreword

This report is a manuscript of a paper which has been accepted for publication in The Journal of Vacuum Science and Technology. The experiment described herein is part of a continuing series of laboratory studies in support of our upper atmospheric program.

Wm. G. Fastie
Research Contract Director
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NsG 193-62

I. Introduction

In order to obtain the emission spectra of the forbidden Vegard-Kaplan band system (lifetime ≈ 1 sec.) of nitrogen, it was found that gas of extremely high purity was required[1]. The most troublesome impurity for our purpose was oxygen, and the reason for this was twofold. First, the oxygen combines with the nitrogen in the discharge to form nitric oxide which is very effective in quenching this forbidden band system by means of collisional deactivation of the $A^3 \Sigma_u^+$ upper state. Second, the overlapping of the very intense β and γ bands of nitric oxide with the Vegard-Kaplan bands makes a fine structure analysis impossible. It was found that the presence of these Vegard-Kaplan bands and the absence of the β and γ bands is an extremely sensitive test for the presence of oxygen--so sensitive, in fact, that oxygen concentrations of much less than one ppm are easily detectable. This is a good example of the power of spectroscopic techniques for the detection of minute impurities.

Other impurities were also noted, but these were relatively easy to eliminate. To our knowledge, a method for obtaining nitrogen of the extreme purity required here has not been previously determined, so that the following investigation was undertaken.

II. Experimental

Using a bakeable ultra-high vacuum system as a basis, various methods for obtaining pure nitrogen were investigated. The purest nitrogen that can be obtained commercially has an oxygen impurity of less than four ppm [2]. Using this in a thoroughly outgassed discharge tube, which was incorporated into the vacuum system, a spectra was obtained which showed no Vegard-Kaplan bands, but in which intense β and γ bands were present. Thus it was evident that much higher purity was required.

It is generally accepted that the purest nitrogen can be obtained by the decomposition of sodium azide; however, this was found to be totally inadequate. Further purification by means of getters was investigated.

The well-known method of using liquid nitrogen cold traps and heated (300^0 C) oxygen-free copper foil was found to be of little help at these low oxygen concentrations. Freshly evaporated films of copper and nickel were also evaluated. The latter was evaporated from a molybdenum boat suspended in a one-liter glass bulb and heated by electrical current. After thorough outgassing, the getter was flashed and a thin film of nickel was deposited on the glass walls. This film is known to selectively absorb O_2, H_2, CO_2, CO, and some hydrocarbons, but not nitrogen, at room temperature.[3] The nickel was more effective than the copper but still not sufficient. A getter of activated uranium[4] was only slightly effective in this case, but in other experiments it was found to be very effective in purifying the rare gases and also as a source of pure hydrogen when used in a slightly different manner.

Two different bulk getters in the form of turnings were investigated. One was zirconium, which was about as effective as the nickel, and the other was a 64 percent zirconium-36 percent titanium alloy which proved to be very successful. This alloy is readily prepared by inert arc melting and can be purchased commercially.[5] It absorbs oxygen more readily than the individual elements, which is probably the result of reduced diffusion barriers within the metal grains. The following procedure proved to be the most effective: The getter was first outgassed by baking at about 1100° C for 24 hours. Then the entire system was baked at 425° C for another 24 hours. This baking process was then repeated once or twice. The final vacuum usually attained with this getter in the system was a few times 10^{-8} mm of mercury. The nitrogen gas was then introduced into the getter tube, which was now heated to about 800° C. After several hours the gas was permitted to flow into the discharge tube. The exact time that the nitrogen is in contact with the getter seems to be of little importance. This alloy also absorbs nitrogen, but at a much slower rate, so that no problems are encountered as long as one starts with a sufficient quantity of nitrogen. It is also effective in the removal of hydrogen, water vapor, the oxides of carbon, and the like. The spectrum of this gas was found to consist of strong Vegard-Kaplan bands whereas the β and γ bands were practically nonexistent, even after very long exposures of 30 hours or more using a 5-meter Fastie spectrograph. Furthermore, no other emissions due to impurities were found in the spectral region investigated. In particular, the intense CN band systems were not found, which indicates that carbon impurities were much less than one ppm. This is also indicative of the effectiveness of the activated alumina trap that was used to isolate the discharge tube and gas handling system from the diffusion pump. Thus this technique is quite adequate for obtaining nitrogen with impurities that should be considerably less than one ppm.

References

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