**NBS TECHNICAL NOTE 496** 

# **Rare Gas Resonance Lamps**

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## **ISSUED OCTOBER 1969**

Nat. Bur. Stand. (U.S.), Tech. Note 496, 55 pages (Oct. 1969) CODEN: NBTNA

## **Rare Gas Resonance Lamps**

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## Contents

	Pa	ige
I.	Introduction	1
II.	General Design Characteristics	4
III.	Procedure for Filling Rare Gas Resonance Lamps	7
IV.	Actinometry	10
	A. Apparatus and Procedure for the Measurement of Saturation Ion Currents	LO
	B. Extinction Coefficients and Ionization Quantum Yields for Various Substances ]	12
v.	Xenon, Krypton and Argon Resonance Lamps	16
	A. Transmission of Windows	16
	B. Operational Characteristics	18
VI.	Helium and Neon Resonance Lamps	20
	A. Aluminum Windows	20
	B. Operational Characteristics	25
	l. Spectral Purity of Helium and Neon Lamps	25
	2. Intensity of Neon and Helium Lamps 2	27
	a) Effect of Helium and Neon Pressure 2	27
	b) Effect of Power and Distance of Discharge from Window	28
VII.	References	30

#### Rare Gas Resonance Lamps

R. Gorden, Jr., R. E. Rebbert and P. Ausloos

Rare gas resonance lamps having high spectral purity, high intensity, and long lifetimes have successfully been manufactured. The design and filling procedure for these lamps is described in detail. Particular operational characteristics of the xenon, krypton, argon, neon, and helium resonance lamps are also given. Windows suitable for use with each of these lamps are described, with particular emphasis given to the procedure for fabricating thin aluminum windows for use with neon and helium lamps. In addition, a method for determining extinction coefficients and ionization quantum yields based on the measurement of saturation ion currents is described.

Key words: Resonance lamps; rare gases; photochemistry; photoionization; extinction coefficients; ionization quantum yield; aluminum window; saturation ion current.

#### I. Introduction

Light sources for use in vacuum ultraviolet photochemistry, photoelectron spectroscopy, as well as other applications, which utilize the emission of the characteristic resonance lines from excited rare gas atoms (see Table I) have now been in use for a number of years.<sup>[1]\*</sup> The rare gas resonance lamps fall into two categories according to their design; namely, those which have windows and those which are windowless. Enclosed lamps, utilizing windows which are transparent in the appropriate wavelength region, are generally fairly simple to make and to use, but until now have been restricted to the energy region including xenon, krypton, and argon resonance radiation because there was no readily available window material

\*Figures in brackets indicate the literature references on page 30

#### Resonance Emission Ionization Energy (eV) (Å) Gas (eV) (Å) He 21.22 584.3 24.59 504.3 Ne 16.85 735.8 21.56 574.9 16.67 743.7 Ar 11.83 1048.2 15.76 786.7 11.62 1066.7 10.64 14.00 Kr 1164.9 885.6 10.03 1235.8 1022.1 9.57 Xe 1295.6 12.13 8.44 1469.6

## Lowest Resonance Emissions and Ionization Energies of the Rare Gases

TABLE I

which would transmit photons of energy higher than 11.8 eV. Windowless lamps, on the other hand, can utilize the rare gases which emit higher energy radiation, but are much more complicated in design since they require differential pumping and impose severe limitations on the pressure of the gas to be irradiated.

It has long been known that certain metals, such as tin or aluminum, or oxides such as SiO, will transmit high energy photons.<sup>[2]</sup> The requirements of nuclear physics and electron microscopy have spurred the development of techniques for forming thin aluminum films supported on very fine mesh screens. If these films are sufficiently thin, yet sufficiently strong, they can be used as windows for rare gas resonance lamps. Recently, the use of such a window on a "continuous plasma" helium lamp was reported;<sup>[3]</sup> the lamp design described in that publication is, however, fairly complicated and difficult to fabricate and use.

In this laboratory, enclosed microwave-operated xenon, krypton, and argon lamps have been in routine use for several years.<sup>[4]</sup> Because of the difficulties in designing a high intensity argon lamp free of impurity radiation, much attention was directed to the development of a simple lamp design which would insure maximum purity of radiation. The result of this effort was a lamp design which successfully incorporates features to minimize impurity radiation, and yet maintains a simplicity which makes it easy to fabricate and use. Lamps made according to this pattern are also found to be very long-lived. Lamp bodies of this design have now been fitted with aluminum windows and enclosed microwave operated neon and helium lamps have successfully been prepared and used.<sup>[5]</sup>

In this report we shall describe in detail the general design for a rare gas resonance lamp which we have found to be most satisfactory and the preferred method of filling such a lamp. We shall then discuss separately the windows and operational characteristics of the low energy (xenon, krypton, and argon) and high energy (neon and helium) rare gas resonance lamps.

#### II. General Design Characteristics

The same basic body design is used for all rare gas resonance lamps. This design is shown in Figure 1. In Figure 2, a possible alternate design which incorporates all the essential features of the lamp is given. The detailed dimensions described below refer to the lamp shown in Figure 1, but it is understood that variations in design, such as those shown in Figure 2, can be made.

The essential features of the lamp (Figure 1), which will be described individually in detail below, are (a) the Pyrex discharge tube, which fits in the cavity of the microwave antenna during operation of the lamp, (b) the window attached to the end of the discharge tube by means of a Ag-AgCl seal<sup>[1]</sup> or epoxy cement, and (c) the Pyrex ballast volume which contains, (d) titanium getter wires connected to nickel leads which pass through a uranium press to the exterior. The getter wires when heated by the passage of a current will deposit a layer of titanium on the interior walls of the lamp, which will effectively remove small amounts of impurities present in the rare gas or knocked out of the Pyrex lamp walls during operation.

The ballast volume, in addition to providing housing for the getter wires, minimizes local heating effects during operation of the lamp and thus improves the stability of the output. In addition, the titanium getter is deposited on the interior surface area of the ballast volume; for efficient removal of impurities, a large area is advantageous. The ballast is a 1000 ml Pyrex volume into which the getter wires have been sealed. In this laboratory, a 20 cm length of 80 mm Pyrex tubing is rounded off at one end and sealed at the other end to the Pyrex flare of the titanium getter assembly.

This assembly consists of seven 0.65 mm-diameter titanium wires, 6.4 cm long, and a heavy common lead connected through a uranium press to external leads. A getter assembly, in which the titanium wires are passed through a teflon flange, is available commercially. It can be directly used in lamp construction if a suitable O-ring assembly is provided to keep the lamp leak-free. The use of the teflon-base getters in this way is not to be recommended, however. Long experience in this laboratory has shown that such lamps invariably begin to emit impurity lines a few days after filling. The recommended procedure is to detach the titanium getter wires from the teflon flange and spot weld them to the interior nickel leads of the commercially available uranium press assembly, whose Pyrex flare can be directly sealed into the ballast volume.

The ballast volume is connected through a short neck to the long discharge tube. In the lamps made in this laboratory, this tube is made of 22 mm diameter tubing, and is about 35 cm in length. As mentioned above, the discharge tube is placed in the cavity of a microwave antenna during operation. The intensity of radiation emitted from the lamp depends on the position of the lamp with respect to the antenna (as well as on other factors that will be discussed later). A wide range of intensity can be achieved by simply moving the microwave antenna along the Pyrex tube toward or away from the window.

Since the lamp is filled with a rare gas through the end of the discharge tube, the tube terminates in some connector for attachment to a vacuum line and requires some provision for closing off or sealing the lamp after it is filled. Thus, the end of the tube may be fitted with a good quality vacuum stopcock, or with a constriction which can, after filling, be heated until it collapses, thus sealing the lamp. The use of a stopcock, lubricated with Apiezon-T grease, has been found to be a satisfactory method of closing a lamp and has the advantage that it provides a ready entry into the lamp whenever refilling is necessary.

In the case of xenon and krypton lamps, which very rarely require refilling, sealing the end of the tube causes little inconvenience, and does eliminate the possibility that small leaks through a stopcock could contaminate the lamp. In the event that the latter course is followed, however, one should be reminded that if the lamp ever does require refilling, it is desirable that it be broken into in such a way that the interior is not exposed to a full atmosphere of air which would contaminate the getter wires and necessitate extensive pumping before the lamp could be refilled. A lamp which is to be sealed can be provided with a breakseal (as shown in Figure 1) which makes it possible to break into the lamp without exposing it to air.

The other end of the discharge tube terminates at the window. The choice of an appropriate window, methods of preparing windows, and attachment of the window to the discharge tube will be discussed below in connection with the descriptions of particular rare gas lamps.

The discharge tube, at a point near the window, is passed through a standard taper joint attached by a ring seal. This provides a convenient means of making a leak-free connection with a reaction cell, a monochromator, a mass spectrometer, or other experimental apparatus. The position of the joint on the body of the lamp, of course, depends on the geometry of the experimental set-up in which the lamp is to be used. For example, for a lamp which is to be used in a reaction cell in which saturation currents are to be measured (Figure 2), the window of the lamp must be positioned between or at least reach the edges of the electrodes if meaningful data are to be obtained.

In earlier rare gas resonance lamp designs reported in the literature, a cold finger was sometimes included so that the impurities could be "frozen out" during operation of the lamp. If the lamp design described here is used, and the filling procedure outlined below is followed, the use of such a cold finger becomes superfluous.

#### III. Procedure for Filling Rare Gas Resonance Lamps

In order to obtain a lamp which is as free as possible of impurity radiation, it is important that the procedure for filling the lamp should have as a major objective the rigorous exclusion of chemical impurities from the lamp. The procedure outlined below is that which has been found to be most successful in this laboratory.

The lamp is filled on a vacuum line which is used exclusively to fill rare gas resonance lamps. This line is never exposed to a high pressure of air, or to any foreign gases. The lamp, when placed on the line, is first rough-pumped through a low vacuum by-pass in order to avoid contaminating the high vacuum manifold with air. The vacuum line is equipped with (a) a two stage oil diffusion pump, (b) a heated manifold onto which reagent grade 1-liter bulbs of the rare gases are sealed, (c) an oil manometer, and (d) a cold cathode gauge.

The body of the lamp is then heated while being pumped down in order to drive impurities off the glass walls. The heating procedure varies, depending on the mode of sealing the window to the body of the lamp. When the window is fastened on with a Ag-AgCl seal, a movable oven is placed around the body of the lamp as it is being evacuated, and the entire lamp is baked at a temperature of 350°C for 24 hours or more. When the window is attached to the lamp body with epoxy cement, the lamp, except for the window area, is repeatedly heated with a torch (about 300-400°C) until further heating does not produce any noticeable increase in pressure, as indicated by the cold cathode gauge. Of course, if a stopcock has been included in the lamp body, it goes without saying that care must be taken to avoid heating the area adjacent to the stopcock.

After the heating procedure is completed, the pressure should be  $10^{-6}$  torr, or lower. At this point, a current of 7 to 8 amps is passed through each of the titanium filaments in turn, in order to de-gas them. A considerable surge of pressure is noted as each filament heats up. The pressure should be allowed to decrease to at least  $10^{-6}$  torr before the voltage is removed from one filament and applied to the next. After all the filaments have been heated, the lamp body is heated again with a torch or when appropriate, by surrounding it with the oven. After a vacuum of  $5 \times 10^{-7}$  is reached, a current of not more than 8.2 amps is passed through one of the titanium getter wires until a thin even layer of titanium is deposited on the inner wall of the ballast volume. This usually takes 30-60 minutes.

The lamp is then filled to the appropriate pressure for the particular rare gas being used (as described later). This pressure is measured on the oil manometer. Immediately after filling, the lamp is sealed off by closing a stopcock or heating a constriction, as discussed above. Approximately five minutes after filling and sealing the lamp, the voltage to the titanium getter is turned off. As an added precaution against introducing impurities into the lamp with the rare gas, a trap can be included between the lamp and the vacuum line and it can be cooled with liquid nitrogen (or acetone-dry ice for a xenon or krypton lamp) just prior to introducing the rare gas.

The emission of xenon, krypton, neon, and helium lamps prepared according to the procedure described above should remain free of impurity lines for long periods of time (over 1,000 hours). The appearance of impurity lines will, however, be accelerated if a) the discharge is brought into contact with the sealing agent used to attach the window to the lamp and b) excessive heating is applied to the pyrex located in the microwave cavity area. In order to minimize the appearance of impurity lines

(mainly the Lyman  $\alpha$  line at 1215.7 Å and the chlorine lines if a Ag-AgCl seal is used) one may resort to the design recently proposed<sup>[6]</sup> which allows the discharge to come close to the window without actually contacting the epoxy or the Ag-AgCl seal. At any rate, as will be demonstrated later, it is not advisable to have the discharge touch the window in many cases. The use of quartz instead of pyrex in the construction of the lamp makes it possible to heat the lamp to higher temperatures during operation without causing excessive liberation of traces of water which may be adsorbed on the surface even after the thorough evacuation techniques described above. Under normal operating conditions, i.e., a discharge more than 1 cm from the window and application of limited power ( $\sim$  10, 20 and 30 watts for a xenon, krypton and argon lamp respectively), one may anticipate that even after 1000 hours of continuous operation 99% of the light emitted by a xenon or krypton lamp in the 1000-2000 Å region is entirely due to rare gas resonance radiation. As far as the argon resonance lamp is concerned, no such degree of success can be claimed. The Lyman  $\alpha$  emission will generally start to show up after 10 to 100 hours of operation. It is, therefore, necessary that such lamps be checked on a monochromator at regular intervals. If the Lyman  $\alpha$  or other impurity line emission appear, it may be removed by heating up one of the titanium getter wires (8.0 amp) until the impurity emission vanishes. This is illustrated in Figure 3 for a particularly bad lamp where the Lyman  $\alpha$  emission is more intense than the argon resonance emission prior to heating the getter. After heating the getter for 60 minutes Lyman  $\alpha$ as well as other lines in 1300-1700 Å region have disappeared. The argon resonance radiation changes only slightly in intensity. It is to be noted that there is no need for refilling the lamp with argon and that the same getter wire can still be used in case the procedure has to be repeated at a later time. It is clear that the same course of action can be used to remove emission lines due to impurities which may build up during operation of the other rare gas resonance lamps. However, as noted above this will generally not be required except perhaps after very extensive usage.

#### IV. Actinometry

## A. Apparatus and Procedure for the Measurement of Saturation Ion Currents

Since most of the conclusions presented in the body of this report will be based on data obtained from measured saturation ion currents, we shall at this point describe the cells in which the measurements are made, and the experimental conditions under which meaningful data are obtained. Finally, as an illustration of the kind of information which can be obtained from this kind of experiment, we shall give some extinction coefficients and ionization efficiencies for various gases, which were derived from saturation ion current measurements.

The ion current measurements are made in a) a reaction cell equipped with two parallel circular nickel electrodes, as that shown in Figure 2, or b) a two-chamber cell<sup>[7]</sup> made according to the design shown in Figure 4. Each cylindrical chamber of the double cell is about 11 cm long and 5 cm in diameter with a volume of approximately 300  $\mathrm{cm}^3$ . In this double cell the two compartments, both of which contain a set of parallel circular nickel electrodes, are separated by an appropriate window---aluminum when the cell is used with neon or helium lamps or lithium fluoride for a cell which is used with argon, krypton or xenon lamps. The gas being investigated is introduced into the cell immediately adjacent to the lamp. The second cell contains a gas which serves as a standard actinometer. In this way, the light transmitted through the material in the first cell can be directly measured, or, when the first cell is empty, the intensity of the lamp can be adjusted to any predetermined value by obtaining the appropriate saturation current in the second cell.

The standard actinometric gas can, in principle, be any gas for which the quantum yield of ionization at the wavelength of interest is known. In practice, experimental errors of measurement can be minimized if the actinometric gas gives a constant saturation current over a wide voltage range. This will be the case for gases which have a low extinction coefficient at the wavelength emitted by the lamp. In this laboratory, NO has been found to be a satisfactory actinometric gas for use with the argon ( $\epsilon \begin{bmatrix} 1067 & A \\ NO \end{bmatrix} = 300$ ) and krypton ( $\epsilon \begin{bmatrix} 1236 & A \\ SO \end{bmatrix} = 57$ ) lamps, while hydrogen is used in the second cell with the neon ( $\epsilon_{H_2}$  = 300) and helium ( $\epsilon_{H_2}$  = 170) lamps.<sup>[9]</sup> The ionization quantum yield of NO at the 1235.8 Å and 1066.7 Å lines is 0.77 and 0.70, respectively. The ionization quantum yield of hydrogen at the neon and helium lines is 0.94 and 1.0, respectively: Argon with an ionization efficiency of one [10] absorbs the neon and helium lines very strongly:  $\epsilon_{Ar}^{740} = 900$ ,  $\epsilon_{Ar}^{584} = 975$ .<sup>[11]</sup>

It can be mentioned at this point that when saturation ion currents are measured in a gas having a high extinction coefficient at the wavelength of the irradiating light, the saturation ion current which is observed is usually obtained over a very short voltage range, and is, therefore, not always well characterized. The plateau of the saturation ion current can be improved by adding to the absorbant gas some other gas which is transparent to the radiation being used. For example, neon is transparent to the helium resonance radiation and it can be used as a diluent for strongly absorbing gases irradiated with the helium lamp. Similarly, helium is transparent to neon resonance radiation, and it can be used as a diluent for irradiations by that lamp. This is illustrated in Figure 5, which shows the saturation current obtained in the same cell and identical intensity of the neon lines in 1 torr of argon as compared to a current obtained in 12 torr of Ar: He (1:14) mixture. The saturation current curve for 5 torr of hydrogen, which is used as a secondary standard because of its weaker absorption, is also given in the figure. The hydrogen and argon pressures are such that 99% of the incident quanta are absorbed. The added helium acts as a moderator, so that cumulative ionization does not occur until higher applied voltages.

In order to obtain good saturation plateaus, as well as meaningful values for the saturation ion currents, the investigator must also be aware of the effects on the measured currents of such parameters as lamp intensity and pressure of the absorbant gas. These effects have been discussed in detail previously, <sup>[7]</sup>, and thus will only be summarized here. Briefly, then, if the number of quanta emitted per unit area of the window is too high, no saturation current can be obtained before cumulative ionization takes place. The saturation ion currents measured for a given sample have been shown to decrease as the pressure of the sample is raised above a given point, presumably because some of the ions undergo recombination with electrons before being collected at the electrode under these conditions. Thus, the investigator should take care to find the optimum conditions of intensity and pressure in order to obtain meaningful saturation ion current measurements.

## B. Extinction Coefficients and Ionization Quantum Yields for Various Substances

Extinction coefficients and ionization quantum yields are easily determined through the measurement of saturation ion currents in irradiated gases.

Quantum yields of ionization  $(\eta_{\mathbf{y}})$  are determined by comparing the saturation ion current  $(i_x)$  obtained in gas (x) at a given intensity with the saturation ion current (ist) obtained at the same intensity in some standard gas whose ionization quantum yield  $(\eta_{st})$  is known at the wavelength of interest. Thus  $\eta_x = \eta_{st} (i_x/i_{st})$ . These measurements are best made at pressures such that all the photons are absorbed by the gases. Ionization quantum yields determined in this laboratory for several gases at the krypton, argon, and neon resonance lines are given in Tables II and III. For the neon lines excess helium was usually added, while for the helium lines excess neon was usually added since, as mentioned before, the plateau of the saturation ion current can be improved by adding a nonabsorbing diluent to the gas of interest. For the measurements at the krypton and argon lines, the standard of comparison was the saturation ion current generated in NO whose ionization quantum yield is known over this wavelength region.<sup>[8]</sup> Xenon, krypton and argon, whose ionization quantum yields are known to be unity  $\begin{bmatrix} 10 \end{bmatrix}$  at the neon and helium lines, were used as primary comparison standards. Hydrogen was used as a secondary standard of comparison since, as shown above, its low extinction coefficient at these wavelengths gives it a well defined saturation ion current.

## TABLE II

Photoionization Quantum Yields ( $\eta$ ) of  $C_4^{H_8}$  Isomers

	I. P.		
	eV	1048-67 Å	<u>1236 Å</u>
Butene-1	9.58	0.321	0.271
Iso-butene	9.23	.31,	.26 <sub>3</sub>
cis-2-Butene	9.13	$.32_{6}$	.255
Methyl cyclopropane	< 10.0	. 440	.172
Cyclobutane	10.3	. 524	. 002

## TABLE III

## Ionization Quantum Yields at Neon Resonance Lines $(735.9 \text{ and } 743.7 \text{ \AA})$

	η		η
CH <sub>4</sub>	1.0	Ar(standard)	1.00
$C_2H_2$	0.92	Хе	1.0
$C_2H_4$	0.9 <sub>8</sub>	H <sub>2</sub>	0.94
$^{C}2^{H}6$	1.0	0 <sub>2</sub>	0.91
с <sub>3</sub> н <sub>8</sub>	1.0	N2	<b>0.9</b> 0
$^{n-C}4^{H}10$	1.0	NO	0.77
$cyclo-C_6^{H}_{12}$	1.0	CO	0.81
с <sub>6</sub> н <sub>6</sub>	1.0	co <sub>2</sub>	0.87
с2 <sup>н</sup> 5 <sup>он</sup>	0.9 2	N <sub>2</sub> O	0.8 <sub>8</sub>
сн <sub>3</sub> сосн <sub>3</sub>	1.0	H <sub>2</sub> O	1.0 <sub>3</sub>
CH <sub>3</sub> I	1.04	H <sub>2</sub> S	1.03
		NH3	0.77

These values were measured with excess helium

(He/X  $\simeq$  20) at total pressure of approximately 20 torr.

The saturation ion current measurements can also be used to obtain the absolute intensity of light entering the cell if the ionization quantum yield  $\eta_x$  for a compound, x, is known and if there is complete absorption of the light by the compound. Thus

$$Q_a = 6.24 \times 10^{18} \left(\frac{1}{\eta_x}\right),$$

where  $Q_a$  is absolute intensity of the absorbed light in quanta sec<sup>-1</sup>, and i, is saturation ion current of x in amperes.

The determination of extinction coefficients using the double chamber cell is quite straightforward. The light transmitted through the evacuated cell ( $T_o$ ) and the light transmitted through the absorbing material (T) at a given pressure are simply proportional to the saturation ion currents,  $I_o$ (saturation ion current with first cell empty) and I (saturation ion current with pressure p in first cell), measured in the second cell. So from Beer's Law, we write:

$$\frac{I}{I_{\circ}} = e^{-\epsilon x p}$$

where x is the path length of the first cell in cm, p is the pressure in atm. and  $\epsilon$  is the extinction coefficient in cm<sup>-1</sup> atm<sup>-1</sup>. The extinction coefficient can also be determined from saturation ion current measurements made in the first cell with the absorbing material. In this case, the incident intensity and the absorbed intensity at a given pressure are simply proportional to the saturation ion currents, I' (saturation ion current for total absorption of the light) and I' (saturation ion current with pressure p), measured in the first cell. Thus we again have from Beer's Law:

$$\frac{I_{\circ} - I_{a}}{I_{\circ}} = e^{-\epsilon xp}$$

Figures 6 and 7 show plots of log  $I/I_{\circ}$  versus pressure measured in the double cell for propane irradiated with the neon lines, and with the helium line. With the neon lamp, calculations made for measurements in the first cell are also included. Again these measurements were obtained with helium or neon added to the propane. In these cases the ratio of the rare gas to

propane was 24. This addition of rare gas, besides enhancing the plateau of the saturation ion current measurements for the first cell, also improved the accuracy of the pressure readings.

The reliability of such measurements is demonstrated by the fact that good straight lines are obtained over a wide pressure range. In addition, the extinction coefficients so obtained ( ${}^{740}_{C_3H_8}{}^{A}_{[12]} = 2950$ ;  ${}^{584}_{C_3H_8}{}^{A}_{[12]} = 2240$ ) are in good agreement with those measured by Schoen.

V. Xenon, Krypton and Argon Resonance Lamps

### A. Transmission of Windows

Xenon resonance lamps are generally provided with LiF or sapphire windows and the transmission characteristics of such windows has been discussed before. [13] Sapphire has the advantage that it only transmits the 1469.6 Å line. However, its transmission of this line is temperature dependent, therefore, LiF may be preferred, especially because the other resonance line at 1295.6 Å is only 2% of that at 1469.6 Å.

For the krypton resonance lamp, on the other hand, the intensity of the high energy resonance line at 1164.9 Å is as high as 25% of that at 1235.8 Å. A 1.5 mm thick  $CaF_2$  window will cut out the 1164.9 Å line (see Figure 8) and may, therefore, be preferred over a LiF window which shows comparable transmission at the two wavelengths. Some care must, however, be exercised if a  $CaF_2$  is used. Figure 9 shows that if the discharge touches the window there will be an exponential decrease of the number of 1235.8 Å photons transmitted through the window as a function of time. The decrease in transmission of the  $CaF_2$  window is apparently only a temporary condition. It can indeed be noticed that if the visible cone of the discharge is moved away from the window (to 4.5 cm) immediately after the fall off, the transmission increases. But, because even at 4.5 cm we notice a slight decrease of the transmission with time, one will not obtain a complete recovery unless the discharge is moved away still further. Only at a distance greater than 6 cm is the percent

transmission independent of the radiation time. This temporary decrease in intensity of the 1235.8 Å resonance line of krypton through a  $CaF_2$  window when the discharge is brought very close is most probably due to a heating effect on the window by the discharge. A similar effect is also noted for the resonance lines of argon through a lithium fluoride window as noted below. The effect of temperature on the transmittance of calcium fluoride and lithium fluoride in the vacuum ultraviolet region, as given in ref. 13, is sufficient to explain these results.

The argon resonance lamp provided with a LiF window will emit the two resonance lines at 1048.2 and 1066.7 Å. Here, however, the percent transmission of the two lines through the window will strongly depend on the thickness and the temperature of the LiF window. This is so because LiF absorbs rather strongly around 1050 Å. The thicker the window the lower the 1048.2 Å/1066.7 Å line ratio will be. For instance, while 1048.2 and 1066.7 Å are transmitted by an argon lamp (Ar pressure = 1 torr) with about equal intensity through a 0.38 mm thick LiF window, the 1048.2 Å line is only 25% of the 1066.7 Å when the window thickness is increased to 1.5 mm. At the same time the total intensity of the two argon resonance lines transmitted through the window will have dropped by a factor of 10.

If the visible discharge is brought close to a 0.38 or 1.5 mm LiF window one notices a sharp drop of the transmission of 1048.2 Å as compared to the 1066.7 Å line. However, just as in the case of the 1235.8 Å transmission through a  $CaF_2$  window, the transmission of 1048.2 Å through the LiF window recovers after the discharge is moved away from the window area. For instance, 1048.2 Å/1066.7 Å intensity ratios of 0.6 and 0.01 were found before and immediately after having brought the discharge within 1 cm of the window. After having the discharge turned off for a few hours the transmitted intensity of the 1048.2 Å line relative to that of the 1066.7 Å line was within a few percent of the starting value of 0.6. It is, therefore, essential that an argon resonance lamp be operated with the discharge at least 5 cm removed from the window. Even so, the transmission of the window will show an exponential drop in transmission as a

function of time (Figure 10). However, in this case the reduced transmission is due to the creation of color centers (F centers) and does not exhibit any recovery upon standing. Also, as noted before [14], the development of color centers diminishes the transmission of the two resonance lines at about the same rate. The transmission of the window can, however, be rejuvenated by bleaching it with a mercury resonance lamp or by heating the window to approximately  $350^{\circ}$ C. The latter procedure can, of course, only be followed if the window is attached to the lamp with a Ag-AgCl seal. In case epoxy cement is used as a sealing agent, care should be taken that the mercury lamp does not cause excessive heating of the window area. If the temperature is allowed to increase to  $60-80^{\circ}$ C considerable strain may develop when the lamp cools down. This sometimes results in cleavage of the LiF window. A blower directed to the window will prevent strain from developing during the bleaching process.

## B. Operational Characteristics

The effect of xenon or krypton pressure on the intensity of these rare gas resonance lamps has already been discussed by Okabe.<sup>[15]</sup> A similar study has been made to establish the optimum argon pressure at which the maximum intensity of the argon resonance lamp is obtained. Two different techniques were used to measure the intensity of the argon lamp as a function of the pressure of argon. In the first method, nitric oxide was used as the actinometric gas in the reaction cell which was equipped with two parallel nickel electrodes. In this case the measured intensity (calculated from the saturation ion current measurement and the ionization quantum yield) is the sum of the intensity of the two resonance lines at 1048 Å and 1067 Å. In the second method, a vacuum monochromator, equipped with a sodium salicylate detector, was used to monitor the relative intensity of the two resonance lines separately.

Figure 11 shows the effect of argon pressure on the relative intensity of each resonance line as well as the pressure effect on the sum of the two resonance lines by method 2. The results of method 1 are essentially identical to this second curve. In obtaining the data by both methods, the position of the microwave antenna with respect to the lamp and the power of the microwave generator were kept constant. Changes in these parameters from one set of experiments to the next produced some variation in the pressure at which the maximum intensity occurred. Thus, from various curves of this nature, it may be concluded that the maximum output in intensity is obtained at an argon pressure between 0.7 and 1.5 torr. It is also to be noticed that there is a second maximum which occurs at an argon pressure from 25 to 7 microns, depending on conditions. This second maximum has considerably less intensity than the first. Figure 12 shows the effect of argon pressure on the ratio of the 1048 Å to the 1067 Å line. [16] Again, if the position of the discharge is moved by changing the antenna, a somewhat different curve is obtained.

This unusual effect of pressure on the relative intensity of the two argon resonance lines has not been reported previously. Moreover a similar effect is not noted for the two krypton resonance lines at 1165 and 1236 Å, whose ratio is relatively constant over the entire pressure range. There are many different parameters which affect the relative intensities of the two resonance lines which emerge from the window of a rare gas resonance lamp and a complete explanation is not practical at this time. However, a partial explanation, at least in the low pressure region (below ~ 0.1 torr), may be related to the large difference in the oscillator strengths of the two argon lines  $(f_{1048}/f_{1067} = 4.1)$  while the oscillator strengths of the two krypton lines are almost equal  $(f_{1165}/f_{1236} = 0.85)$ .<sup>[17]</sup> Thus for an argon resonance lamp in the low pressure region where "pressure broadening" is less important, there is less resonance absorption of the 1067 Å radiation as compared to the 1048 Å radiation. In this connection it is interesting to note that the addition of neon or helium to a low

pressure argon lamp results in an increase in the ratio of 1048 Å/1067 Å. This is to be expected since the added gas gives rise to a "pressure broadening" of the emitted resonance lines and consequently there will be less self-absorption within the lamp. Moreover if the discharge for a low pressure argon lamp is brought closer to the window, the ratio of 1048 Å/1067 Å should increase as seen in Figure 13. For a krypton lamp the two resonance lines are absorbed to almost the same extent and consequently, there is very little difference in the ratio of 1165 Å/1236 Å, as the discharge is brought closer to the window.

Table IV gives an idea of the absolute intensity that can be obtained with the argon resonance lamp with different power settings on the microwave generator and with the discharge at various distances from the window. Somewhat higher intensities than  $10^{14}$  quanta/sec<sup>-1</sup> could be obtained by bringing the discharge closer to the window but, as mentioned before, this would result in a very fast decay because of the heating effect on the lithium fluoride window. In addition, the higher intensity leads to the more rapid formation of F centers in the lithium fluoride window which absorbs the argon lines. Figure 10 shows the decay of argon lamp due to the formation of F centers even at an initial intensity of about  $10^{13}$ quanta sec<sup>-1</sup>.

### VI. Helium and Neon Resonance Lamps

#### A. Aluminum Windows

The 21.2 eV (584.4 Å) helium resonance line and the 16.7-16.8 eV (735.9 - 743.7 Å) neon resonance lines can be transmitted to an appreciable extent through aluminum. For instance, a film of aluminum 1000 Å thick with a layer of aluminum oxide 40 Å thick on each surface will transmit 26% of the 21.2 eV helium line, or 9% of the 16.7 eV neon line. <sup>[18]</sup> Thus, aluminum is a suitable window material for a helium or neon resonance lamp. There are several other materials which transmit radiation in this wavelength region, but aluminum presents certain advantages over these. For example, thin (1000 Å - 4000 Å) foils made of aluminum exhibit a mechanical

## TABLE IV

## Intensity of the Argon Lamp<sup>a</sup>

Power	Distance <sup>b</sup>	Intensity
(%)	(cm)	(photons $\sec^{-1} \times 10^{-13}$ )
10	9.0	2.9
20	7.0	4.8
38	4.5	9.7
50	3.0	11.2
	0	

<sup>a</sup>Pressure of argon in lamp = 1.0 torr.

<sup>b</sup>This is the distance of the discharge from the window.

strength and rigidity which is beneficial for window construction. Another advantage of using aluminum is that it shows a sharp decrease in transmission for photons of energy below 15.5 eV. This means that an aluminum window will filter out low energy impurity radiation such as the Lyman  $\alpha$  line of hydrogen. These persistent impurity lines are a great nuisance in the lower energy lamps---particularly in argon lamps---where they are not so simply eliminated. However, the fact that the window filters out low energy impurities does not necessarily mean that precautions to exclude these impurities should be abandoned. The presence of large amounts of impurities in the lamp will necessarily mean a decrease in the intensity of the helium or neon radiation emitted, as energy transfer to the impurity molecule would be very efficient.

A schematic diagram of the aluminum window assembly is shown in Figure 14. In our studies, aluminum films (a) of 1000 Å, 2000 Å, and 4000 Å thickness were used. The aluminum is supported by an electroformed nickel mesh (M) of 100 lines per inch, which has a transparency of 82%. The mesh is first spot welded to a steel washer of diameter at least as great as that of the discharge tube of the lamp to which it will be joined. The aluminum film is applied using a procedure similar to that recently described. [19] That is, the aluminum is evaporated in a molecular furnace to form an even layer of the desired thickness on a glass slide which has previously been covered with a layer of sodium chloride. A circular segment of the proper size, which is to be used as the window, is then cut out by carefully rotating a circular cutter (similar in design to a large cork-bore) on the surface of the film. The slide containing the aluminum film is then slowly dipped into the distilled water at an angle of approximately 30°. The aluminum film will detach itself from the slide and float on the surface of the water. It is essential that the film starts to float as the lower edge of the aluminum window dips into the water. The meshwasher assembly, in the meantime, has been dipped into a dilute solution  $(\sim 0.5\%)$  of formvar in ethylene dichloride, and the ethylene dichloride solvent has been allowed to evaporate. The mesh-washer assembly is then dipped into the water and brought in contact with the aluminum at one edge. The aluminum film adheres to the mesh-washer assembly as it is lifted from

 $\mathbf{22}$ 

the water in a vertical plane. If one is dissatisfied with the smoothness of the window obtained in this way, the aluminum film can be refloated by lowering the assembly in a vertical plane back into the water, and then the lifting procedure can be followed a second time. The window is then exposed to the vapor of ethylene dichloride in order to soften the formvar and effect a seal between the mesh and the aluminum film.

At this stage, it is necessary to carefully examine the window through a low power microscope for small pinholes. Pinholes are readily discernible if a bright light is placed below the window and the examination is carried out in a darkened room. Such pinholes can be plugged with any kind of sealing agent which can be applied at room temperature with, say, one soft bristle from a brush.

The window assembly is then attached to the rim of the Pyrex discharge tube of the lamp. Vacuum epoxy cement or some other low vapor pressure sealing agent which can be applied at room temperature may be used for this purpose. The lamp is then inserted into the reaction cell, or other apparatus with which it is to be used, preparatory to filling.

Because the aluminum window can generally not withstand a pressure differential greater than 100 torr, the lamp fitted with an aluminum window requires some special handling during and after filling. Prior to filling, the lamp and the apparatus in which it is inserted must be evacuated simultaneously. After the pressure has been reduced to a few microns, the lamp (accompanied by its evacuated apparatus) can be attached to the special vacuum line for filling as described in the previous section. Again, after filling, care must always be taken that the pressure differential to which the window is exposed does not exceed the 100 torr limit. The actual pressure differential toleration of the window will depend on several factors such as the thickness of the aluminum film and the structure of the supporting mesh. In addition, imperfections in the aluminum surface may lead to localized ruptures when the pressure is raised to a certain level. Such localized

pinholes at weak spots are most often observed when the pressure is gradually increased. A sudden high pressure of gas applied to the window will, of course, result in a uniform puncturing over the entire window area.

In filling a helium or neon lamp for use with the double cell mentioned earlier, it is imperative that all three sections (the lamp, the first cell, and the second cell) are evacuated simultaneously. Since aluminum windows must be used to separate each section, no large pressure differential can be tolerated between any two compartments. Moreover in using this double cell arrangement, it is also well to remember that the transmission characteristics of the central aluminum window differ for the helium and neon resonance radiation. When a helium lamp operating at a certain intensity is replaced by a neon lamp, and the intensity is adjusted so that the number of photons per second entering the first cell is identical to that of the helium lamp. it is found that only 20% as much radiation passes through the evacuated first cell and the 1000 Å aluminum window into the second cell. A similar ratio of transmission can be estimated for the light passing through a 1000 Å aluminum window attached to a lamp, when the helium in the lamp is replaced by neon. Madden et al<sup>[18]</sup> have measured the transmission of the neon and helium resonance lines through aluminum films of various thicknesses having a 40 Å oxide layer on each surface. They report that a 2000 Å film transmits only 18% as much neon as helium resonance radiation. As mentioned above, he finds that a 1000 Å aluminum film covered by a 40 Å layer of aluminum oxide on each surface, transmits about 35% as much neon as helium resonance radiation.

#### B. Operational Characteristics

We shall now discuss the spectral purity and the intensity of the neon and helium resonance lamps.

1. Spectral Purity of Helium and Neon Lamps

In order to characterize the energies of the lines emitted by the neon and helium resonance lamps, we measure the amount of ionization caused by absorption of these lines in the rare gases, xenon, krypton, argon and neon. Samson<sup>[10]</sup> has shown that when a rare gas absorbs a photon of energy higher than its ionization potential, it invariably undergoes ionization, hence, its ionization quantum yield is unity. Thus, it is not surprising that for a given (helium or neon) lamp operating at a constant intensity, the ion currents measured in xenon (I. P. = 12.1 eV), krypton (I. P. = 14.0 eV) or argon (I. P. = 15.7 eV) samples are identical, if the pressure of the absorbing gas is such that all quanta of light are absorbed. This result confirms that no photons of energy lower than 15.9 eV  $(Ar^+, {}^{2}P_{1/2})$  enter the reaction vessel from a helium or neon lamp since, if photons of energy between 12.1 eV and 15.9 eV were present, the ion current measured in xenon would have been higher than that measured in argon. Photons of energy lower than 12.1 eV are not transmitted through an aluminum window. The absence of photons with energies lower than 15.9 eV in the emission from the helium lamp is further confirmed by the observation that the saturation ion current measurements obtained in NO, when compared with the currents measured in the rare gases, indicate that the quantum yield of ionization in NO at this wavelength is  $0.95 \pm 0.02$ . This is in good agreement with the value of 0.94 reported by Watanabe et al.<sup>[8]</sup> at an energy of 21.28 eV.

The emission from the helium and neon lamps does not, on the other hand, include any photons of energy as high at 21.5 eV. This is demonstrated by the fact that when neon (I. P. = 21.5 eV) is placed in the cell and irradiated with either the helium or neon lines, no ionization is observed.

It should be mentioned at this point that no gases except helium and neon emit photons exclusively at energies between 15.9 and 21.5 eV. The discharge from these lamps can be more conclusively characterized, however, by introducing neon and helium themselves into the double cell and observing whether or not the emission from these two lamps is absorbed by these gases. A rare gas will, of course, absorb its own resonance line. Thus we see that neon does absorb the radiation emitted by the neon resonance line (see Figure 15). but is entirely transparent to the emission of the helium resonance lamp. Similarly, helium absorbs the radiation emitted by the helium resonance lamp (see Figure 16), but is transparent to the emission of the neon resonance lamp. Thus, we can conclude that the helium and neon resonance lamps are completely characterized. The only helium resonance line between 15.9 - 21.5 eV is the one at 21.2 eV (584.4 Å). For neon there are two resonance lines. One is at 16.8 eV (735.9 Å) and the other is at 16.7 eV (743.7 Å). The ratio of the intensity of 735.9 Å to 743.7 Å is given as 2.5 by Boyce<sup>[20]</sup> who used an electrodless discharge and as 3.3 by Samson<sup>[21]</sup> in a duoplasmatron. In our system the selective absorption by the aluminum window will increase this ratio somewhat for the radiation coming out of the lamp.

It may be added that the above observations also indicate that the neon, which according to the manufacturer may be present in the helium at a concentration of 5 ppm or less, is not present in sufficient quantity to provoke appreciable energy transfer from helium to neon in the lamp during operation. This is further confirmed by a visual observation of the color of the helium discharge which is whitish-pink rather than the characterisitc deep red color of the neon discharge.

In connection with the resonance absorption mentioned above, it should be noted that there is a reversal of the resonance light which actually comes out of the rare gas resonance lamps. This is due to the absorption of the resonance photons by the rare gas within the lamp. The degree of reversal depends on the pressure of gas in the lamp and the distance of the discharge

from the window. This is graphically illustrated by the results given in Figures 15 and 16. It is apparent that the extinction coefficient of neon for the neon resonance radiation increases as the pressure of neon in the lamp is decreased. This same effect occurs when the discharge in the neon lamp is brought closer to the window, i. e., there is a higher extinction coefficient when the discharge is close to the window than when the discharge is far from the window. This is seen in Figure 16 for the absorption of the helium resonance radiation by helium. Effects of this nature are discussed in detail by Braun and Carrington.<sup>[22]</sup>

#### 2. Intensity of Neon and Helium Resonance Lamps

#### a) Effect of helium and neon pressure

An attempt was made to establish the optimum helium or neon pressure at which a lamp should be filled in order to obtain maximum intensity at constant power. Several plots which represent the saturation ion current measured in hydrogen versus the pressure of helium or neon in the lamp are given in Figures 17, 18 and 19. In obtaining the data for these curves, the position of the microwave antenna with respect to the lamp and the power of the microwave generator were kept constant. In the case of the helium lamps, there is no significant difference in the visible discharge as the pressure in the lamp is changed, but in the case of the neon lamps the discharge was observed to expand slightly as the pressure decreased. Therefore, a series of measurements (Figure 19) were carried out on the neon lamps in which the power of the microwave generator was kept constant, but the position of the antenna was changed so that the visible discharge would remain a constant distance from the window. It may be concluded from the data, given in Figures 17 and 18, that for a helium lamp the maximum output of radiation will be obtained when the pressure of gas in the lamp is between 1.2 and 2 torr. For a neon lamp, the data in Figure 19 show that the maximum output at constant power is obtained at gas pressures of about 2 torr.

#### b) Effect of power and distance of discharge from the window.

When the position of the antenna with respect to the lamp is kept constant, and increasing amounts of microwave power are supplied, there is, as one would expect, an expansion of the region in which the visible discharge glow is observed. A measurement of the saturation current in hydrogen as a function of increasing power is shown in Figure 20 for the neon lamp. We see that the intensity of the lamp apparently increases exponentially with the power. However, a comparison of the results obtained with the helium and the neon lamps shows that while an increase in power from 10 to 40% results in nearly a tenfold increase in intensity of the neon lamp, the helium lamp increases in intensity by less than a factor of two over this power range (see Figure 21). This difference can largely be ascribed to the fact that the visible discharge region of the helium lamp does not expand as rapidly with increasing power as does the visible discharge of the neon lamp. The sharp increase in output of the neon lamp as a function of power is largely due to the fact that the discharge region, in expanding, comes nearer to the window. In another set of measurements with the neon lamp, the power is increased while the position of the antenna is adapted so that the region of the visible discharge remains at a constant distance from the window. Under these conditions, less than a twofold increase in intensity is seen when the power is raised from 5 to 50%.

Similarly, in Figures 21 and 22 which give the results of experiments performed with a helium lamp fitted with an aluminum window 2000 Å thick, we see that the intensity of emitted radiation increases when (1) the power is increased while the visible discharge is kept at a constant distance from the window, and (2) when the power is kept constant, but the visible discharge region is brought closer to the window.

 $\mathbf{28}$ 

The absolute intensity of these helium and neon resonance lamps depends, as we have seen, on many factors such as: the pressure of rare gas in the lamp, the power of the microwave generator, the distance of the discharge from the window, and trace impurities in the lamp. Under optimum conditions a freshly prepared helium lamp ( $\sim$  1.7 torr helium), with a 1000 Å thick aluminum window of about 2  $cm^2$  area, can produce an intensity of approximately 3 x  $10^{14}$  guanta sec<sup>-1</sup>. Under similar conditions a neon lamp will have an optimum intensity of approximately 7 x  $10^{13}$  quanta sec<sup>-1</sup>. Such high intensities, however, seem to result in a rather rapid decay of the aluminum window. If the intensity is reduced a constant output is obtained for many hours. In one set of measurements the intensity of a neon lamp (1000 Å aluminum window, 2.1 torr neon) decreased from  $1 \times 10^{13}$  guanta  $sec^{-1}$  to 0.8 x 10<sup>13</sup> guanta sec<sup>-1</sup> in one hour. However, there was no noticeable decay of the lamp in the same time period when the initial intensity was reduced to  $1 \times 10^{12}$  quanta sec<sup>-1</sup>. Likewise for the helium lamp, after one hour the intensity dropped from  $4 \times 10^{13}$  quanta sec<sup>-1</sup> to 3 x  $10^{13}$  guanta sec<sup>-1</sup>. Again, when the initial intensity was reduced to  $1 \times 10^{12}$  guanta sec<sup>-1</sup>, it took five days of continuous irradiation before the intensity decreased to  $0.5 \times 10^{12}$  quanta sec<sup>-1</sup>. The rapid initial decrease of intensity with time is due mainly to a decrease in tramsmission of the aluminum window, since refilling the lamp or firing one of the titanium getters results in only a slight increase in intensity. This decrease in transmission of the aluminum window is most probably due to some changes in the aluminum oxide surface layer, which at 584 and 740 Å has a much higher extinction coefficient than the aluminum itself. It is not possible to say at this time whether there is a contaminant forming on the surface, if the oxide layer is increasing in thickness, or if there is a physical change in the oxide layer due to the action of high energy photons.

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Figure 1. The basic design of the rare gas resonance lamp.



- The rare gas resonance lamp attached to a photolysis cell. Figure 2.
- titanium getter wires in the 1000 cc ballast volume; I
- microwave cavity; u ∩ ≥ H
  - ī
- window; nickel electrodes. I



Figure 3. Monochromator record of the radiation from an argon resonance lamp.

----- Before heating the titanium getter; ------ After heating the titanium getter for 60 minutes.



Figure 4. A double cell arrangement for actinometric measurements. L - resonance lamp; E and E<sub>2</sub> - nickel electrodes; W<sub>1</sub> and W<sub>2</sub> - lithium fluoride, calcium fluoride or aluminum windows; P - pyrex disc; O and S - viton "o" rings and glass separators, respectively through which the interelectrode distance is varied; J - a standard type joint 34/45.





A plot of  $I/I_0$  versus the propane pressure for the neon resonance lamp. Figure 6.

0 - measurements of I/I made in second cell;  $\Box$  - measurements of  $I_0' - I_a'/I_0'$  made in first cell.



Figure 7. A plot of I/I versus the propane pressure for the helium resonance lamp.





Heating effect on the transmission of 1.5 mm  ${\rm CaF}_2$  window for the 1236 Å line of Kr. Figure 9.

- decrease with discharge against window; O recovery with discharge 4.5 cm from window;  $\Delta$  decrease with discharge 4.5 cm from window.







Effect of pressure on the ratio of  $1048/1067~{\rm \AA}$  lines from an argon resonance lamp. Curves F and C simply reflect different antenna positions and powers. Figure 12.





Figure 14. Schematic diagram of the aluminum window assembly.

- A aluminum window 1000, 2000 or 4000 Å thick;
- M nickel mesh of 100 lines per inch and 82% transparent;
- W stainless steel washer, 25 mm O.D. and 16 mm I.D.; P pyrex discharge tube of the lamp.







- A plot of intensity of the helium resonance lamp (4000 Å aluminum window) versus the pressure of helium. Figure 17.
  - 0 30% power, antenna 10 cm from window; 40% power, antenna 20 cm from window.
- In this and in the subsequent figures the saturation current is measured in hydrogen.





 $\Delta$  - 40% power, antenna 10 cm from window; 0 - 20% power, antenna 20 cm from window.





Figure 20. A log plot of the intensity of the neon resoance lamp versus power with antenna 20 cm from the window.

0 - 4000 Å aluminum window;  $\Delta$  - 1000 Å aluminum window.









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NOTE: This schematic is neither an organization chart nor a program outline for budget purposes. It is a general statement of the Department's mission in relation to the national goal of economic development.

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