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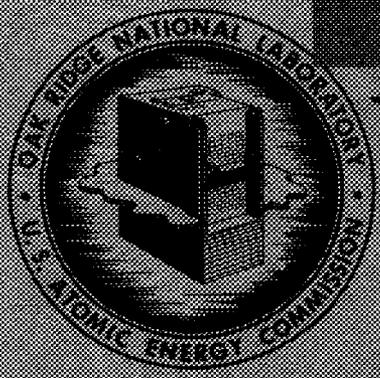
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A STUDY OF ALPHA PARTICLE
IONIZATION IN ARGON MIXTURES

F. W. Sanders
G. S. Hurst
T. E. Bartner

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A STUDY OF ALPHA PARTICLE IONIZATION IN ARGON MIXTURES

F. W. Sanders, G. S. Hurst, and T. E. Bortner

HEALTH PHYSICS DIVISION

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1. INTRODUCTION

When an alpha particle passes through a gas it may form an ion by acting on atoms or molecules of the gas with enough force to remove an electron. The value of W , which is the average energy required to produce an ion pair, is found to be greater than the lowest ionization potential of a given gas. The reason for this is that the energy considered in calculating W goes not only into ionization but also into excitation of non-ionized atoms or molecules and into kinetic energy of the electrons removed in ionization.

The addition of certain impurities to some of the noble gases reduces the value of W considerably¹ and the results of separate additions to argon of seventeen gases have been measured.² These gases have a range of ionization potentials from 8.5 to 15.7 electron volts (ev). The ionization potential of argon is 15.68 ev. Included were gases with ionization potentials above and below the known metastable excited state of argon, 11.5 ev. Many observers had believed that the reduction of W , or increased ionization, was caused by the discharge of the metastable state; however, the increased ionization effect was observed using impurities with ionization potentials above the metastable level. The highest ionization potential at which the effect was noted was 14.5 ev;

1 T. E. Bortner and G. S. Hurst, Phys. Rev. 90, 160 (1953).

2 C. E. Melton, "Measurement of Ionization Produced by 5-Mev Alpha Particles in Argon Mixtures," A Thesis, Vanderbilt University (February 1954).

with an impurity having an ionization potential of 15.5 ev there was no increase detected.

This study was undertaken to investigate the cause of the increased ionization in mixtures of argon and impurities with ionization potentials above the argon metastable level, 11.5 ev.

Three mechanisms for the increase of ionization by impurities with ionization potentials in the 11.5 to 14.5 ev range have been suggested. The increase could be due to (1) the discharge of a metastable excited level of molecular argon, (2) the action of subexcitation³ electrons, i.e. electrons with kinetic energy less than the lowest excited level of argon, or (3) the discharge of a long lived excited state of atomic argon with an energy level greater than 14.5 ev. Experiments were undertaken to determine which, if any, of these suggested mechanisms accounts for the increased ionization.

If molecular argon exists, its concentration and therefore its effect on ionization will depend on the pressure of the gas. The effect of a 725 mm of Hg change of gas pressure on the increased ionization was studied using a large parallel plate ionization chamber containing a Pu^{239} alpha source.

The energy distribution of subexcitation electrons, and therefore their effect on the ionization process, is altered by changing E/P (the ratio of change of potential per unit distance to pressure in volts/cm/mm Hg).³ The effects of large changes of E/P were studied in the

³ R. L. Platzman, Rad. Res. 2, 1 (1955).

ionization chamber.

An optical spectrograph was used in conjunction with ionization chamber data to study the possibility of a long lived excited state of atomic argon. The emission spectrum of pure argon was compared to the spectra of mixtures of argon and ethane, propane, acetylene, and nitrogen. This parallel study was based on the assumption that the same events of interest occur in the ionization chamber and in the exposure chamber of the spectrograph.

II. APPARATUS

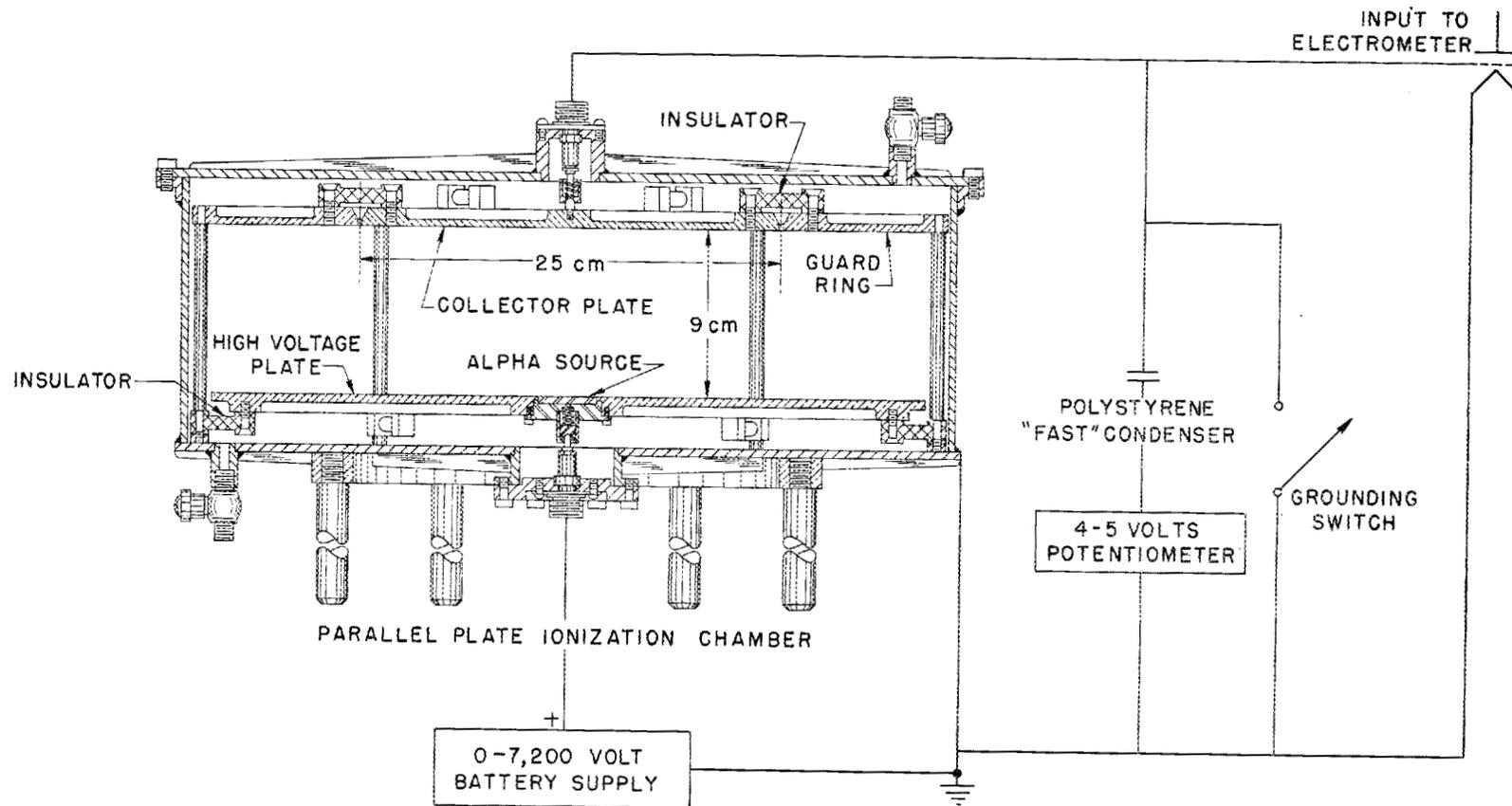
The apparatus might be divided into two categories: that for the study of the effect of changes of E/P and gas pressure on ionization, and that for the study of the effects of impurities on the emission spectrum of argon.

Apparatus for Ionization Study

The apparatus used for the ionization versus pressure and the ionization versus voltage studies consisted of a large ionization chamber with an uncollimated internal Pu^{239} alpha source and associated vacuum system, a high voltage supply, a potentiometer, a capacitor and a vibrating reed electrometer.

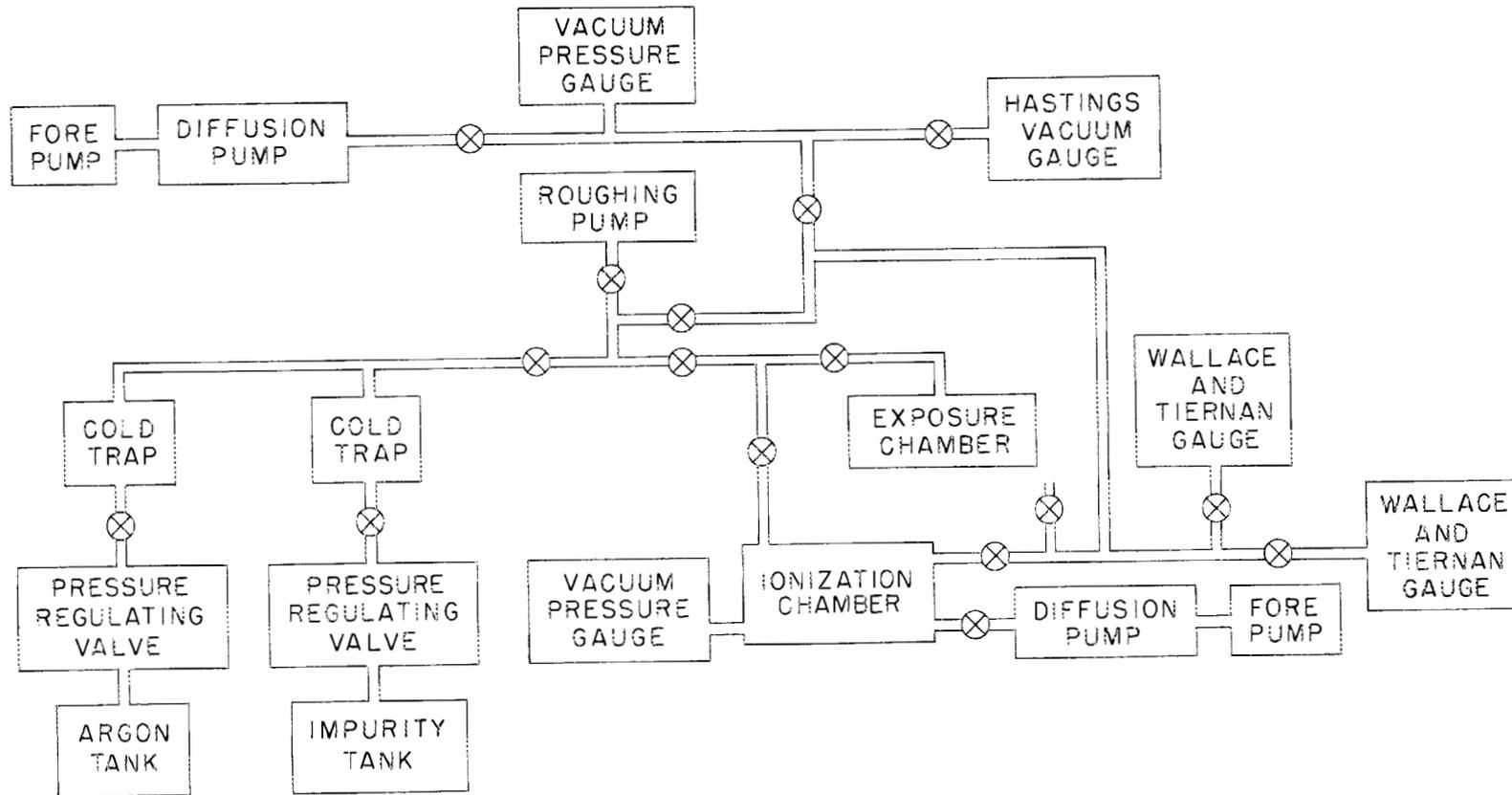
The parallel plate ionization chamber (Fig. 1) was enclosed in a steel cylinder 50 cm in diameter and 15 cm high. The 24S aluminum plates were supported 9 cm apart by Teflon insulators. The collecting plate was 25 cm in diameter and was surrounded by a guard ring with a clearance of 0.030 cm. The high voltage plate, which contained the Pu^{239} alpha source flush mounted in its center, was 46 cm in diameter.

The remainder of the gas system (Fig. 2) consisted of two vacuum-pressure gauges, a Hastings vacuum gauge, two Wallace and Tiernan vacuum gauges, three mechanical pumps, two diffusion pumps, and two cold traps. One of the Wallace and Tiernan gauges had a range of 0 to 200 mm of Hg, and the other a range of 0 to 800 mm of Hg. The diffusion pumps



5

FIG. 1. BLOCK DIAGRAM OF THE APPARATUS FOR MEASURING W FOR ALPHA PARTICLES



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FIG. 2. BLOCK DIAGRAM OF THE GAS SYSTEM

were VFM model 260, oil diffusion pumps manufactured by Distillation Products Corporation. The mechanical pumps were Welch Duo-Seal, two of which were used as forepumps in series with the diffusion pumps and one of which was used as a by-pass pump to allow removal of gases that might contain oxygen which would oxidize hot diffusion pump oil. The cold traps were brass cylinders 4.5 cm in diameter and 16.5 cm in height. With the exception of the connections to the diffusion pumps, where one inch and three-fourths inch nickel tubing was used, the components of the system were connected with one-fourth inch copper tubing.

Two high voltage supplies were used. For potentials greater than 300 volts a supply consisting of series connected 300 volt batteries was used. The high voltage plate was connected to the series' positive terminal and the desired voltage was obtained by connecting the ground lead to the negative terminal of the proper battery. For potentials less than 300 volts, a stable regulated high voltage supply manufactured by the Oregon Electric Company was used.

The potentiometer, which was designed for use with this equipment by the Instrument Department of the Oak Ridge National Laboratory, had a reference voltage output that was variable from 0 to 4500 millivolts. It was monitored at five points with a Rubicon potentiometer.

A "Fast" capacitor manufactured by John E. Fast Company was used as the collecting capacitor.

An Applied Physics Corporation model 30 vibrating reed electrometer was used as a null indicator. The instrument had a background drift

rate of less than one millivolt per minute which was negligible compared to the signal drift rate.

Apparatus for Spectrum Study

The apparatus used for studying the effect of impurities in argon on the emission spectrum of argon consisted of a gas mixing and filling system, an exposure chamber, a spark source, a spectrograph, film and a recording microphotometer.

The gas system and ionization chamber previously described were used for preparing gas mixtures and filling the exposure chamber. This system was used because it was convenient and because its large capacity enhanced the accuracy of the admixing of a small percentage of impurity. The exposure chamber could be connected directly to this system.

The exposure chamber (Fig. 3) consisted of a pipe tee of 6.3 cm inside diameter. The opposed openings were fitted with Teflon plugs which supported screw advancing electrode holders. The distance between the electrodes could be adjusted while a gas sample was in the chamber. The electrodes, which were of spectroscopically pure magnesium, were maintained 8 mm apart during operation. The third opening had a Teflon plug fitted with a quartz window 2.5 cm in diameter and 3 mm thick.

The spark source was manufactured by Applied Research Laboratories-Henry W. Dietart Company. It was used at a power level of 2 KVA and was connected by cables to the electrode holders of the exposure chamber.

A Bausch and Lomb 1.5 meter stigmatic grating spectrograph was used. The dispersion of this instrument was $15 \text{ \AA}/\text{mm}$ in the first order

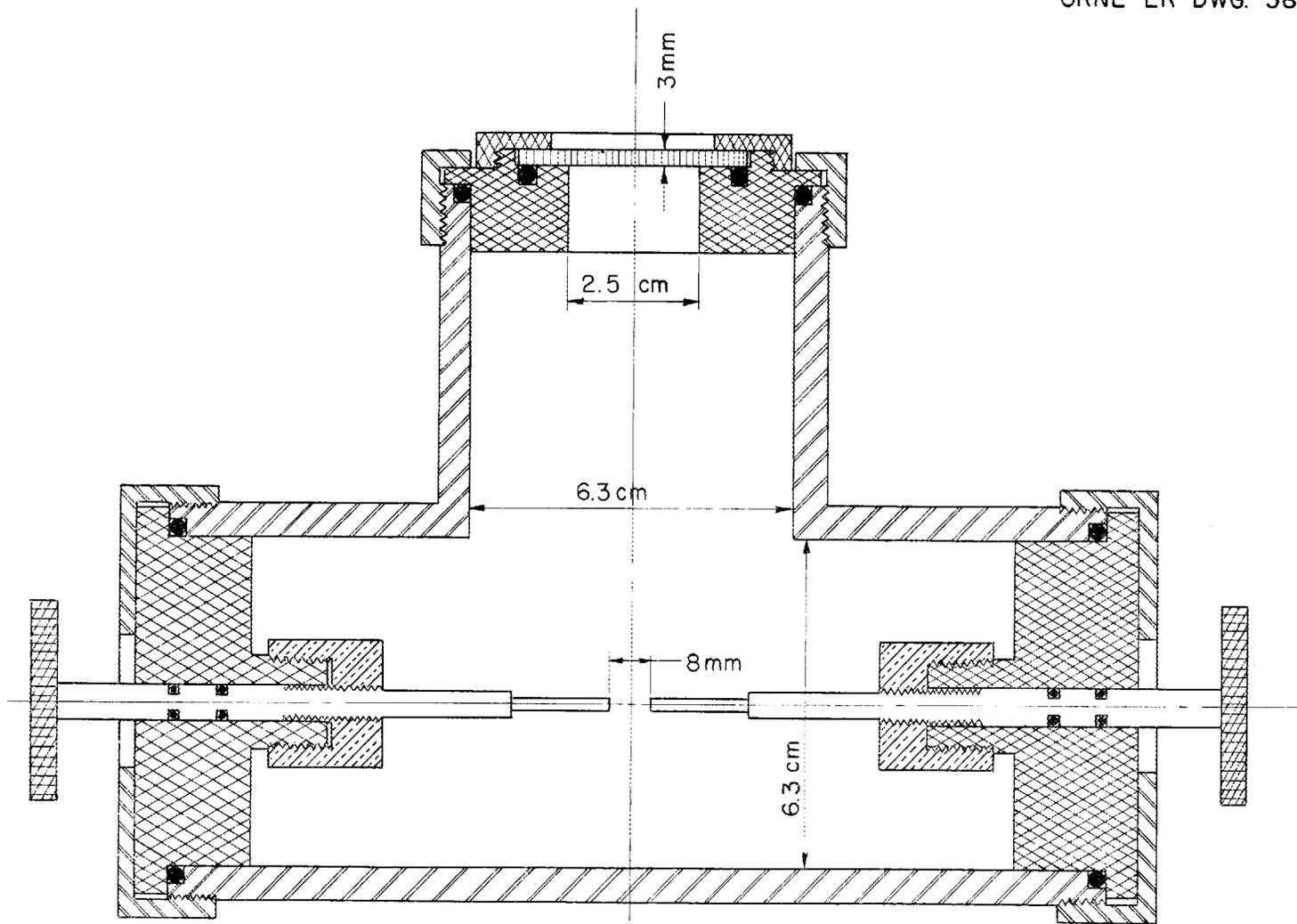


FIG. 3. DIAGRAM OF EXPOSURE CHAMBER

and 7.5 \AA/mm in the second order. Eastman Spectrographic Safety Film, type I-L, which covers the visible range plus the near ultraviolet, was used in the spectrograph. The recording microphotometer used was a Leeds and Northrup model 6700-A1, with a Speedomax recorder.

III. PROCEDURE

In order to remove impurities, especially water vapor, all gases studied were purified by flowing slowly through a dry ice cold trap. Argon purified in this manner showed a purity of 99.9% when analyzed with a mass spectrograph. Prior to filling, the entire gas system was flushed with argon and pumped to a pressure of less than 10^{-3} mm of Hg, the smallest unit registered by the Hastings vacuum gauge used. All fillings were made to a pressure of 750 mm of Hg. When pure argon was used, the chamber was flushed for ten minutes and then pumped to 750 mm of Hg and sealed. When a mixture of gases was used, argon was admitted to the proper partial pressure, the chamber sealed, the remainder of the system evacuated and flushed three times with the correct impurity, and the impurity was then admitted to the chamber to complete the 750 mm of Hg total pressure. Impurities used included ethane (C_2H_6), propane (C_3H_8), acetylene (C_2H_2), and nitrogen (N_2). The percentages of impurity² used were those which gave the greatest lowering of W except those for nitrogen, which showed no lowering effect, and for one series of argon-ethane measurements. Percentages used were: ethane, 3% and 1%; propane, 3%; nitrogen, 3%; and acetylene, 0.5%. Maximum lowering of W for argon-ethane is at 3% ethane.

To insure complete collection of the ions formed, saturation curves (Fig. 4) were determined at 750 mm of Hg pressure for each gas mixture to be tested and for pure argon. In all cases saturation occurred below 300 volts. For this chamber the number of ions collected at voltages

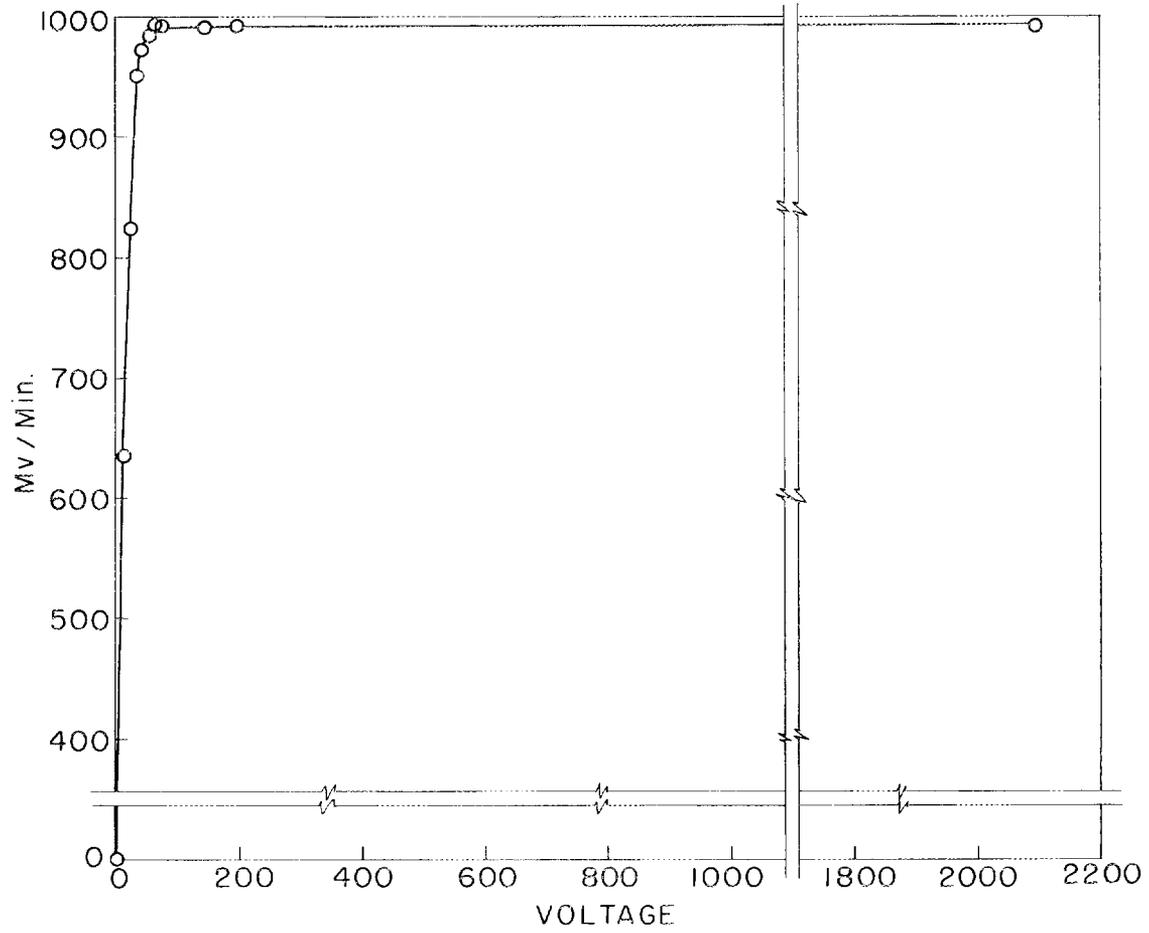
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FIG. 4. IONIZATION VERSUS PLATE VOLTAGE FOR 97% ARGON-3% ETHANE MIXTURE AT 750 mm Hg PRESSURE

above the saturation voltage was constant up to the potential at which high voltage breakdown occurred. At this potential, measurements could no longer be made because of obvious fluctuations of the electrometer. Voltage used at 750 mm of Hg pressure was 2100 volts.

Because the potential at which high voltage discharge starts becomes much lower at lowered pressure a chamber of each gas mixture was slowly pumped down until the discharge started. The pressure above which that voltage could be safely used was noted (Fig. 5), the voltage was lowered 300 volts, and the pump down was continued. This calibration insured that the voltage used was always well above the saturation and below the discharge potential.

The final measurements were made at gas pressures which ranged stepwise from 750 mm of Hg to 10 mm of Hg. The variable measured was the length of time required to charge the capacitor to a predetermined voltage.

A formula for determining W can be derived easily by using the following notation:

- e - charge of the electron, in coulombs;
- E - average energy of the alpha particles, in electron volts;
- N - number of Pu^{239} disintegrations per minute;
- C - capacitance of the capacitor, in farads;
- V - potential of the capacitor, in volts;
- dV - change in potential;
- Q - charge on the capacitor, in coulombs;

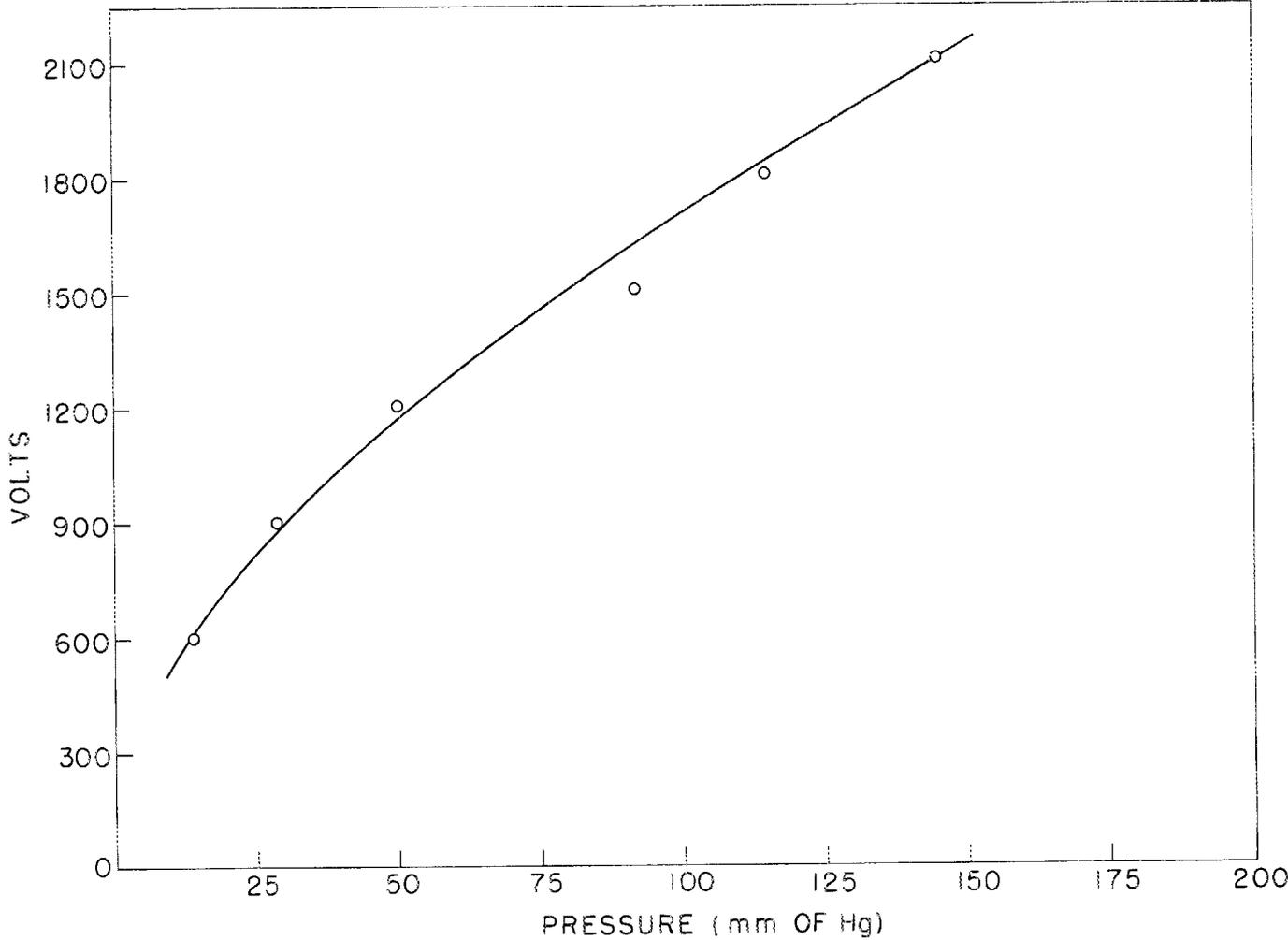


FIG. 5. BREAKDOWN VOLTAGE VERSUS PRESSURE OF 97% ARGON-3% ETHANE MIXTURE.

dQ - change in charge;

W - average energy required to produce an ion pair, in electron volts.

The total energy loss per minute of the alpha particles in the gas is NE .

$$Q = CV \quad (1)$$

so the rate of change of charge on the capacitor is

$$\frac{dQ}{dt} = C \frac{dV}{dt} \quad (2)$$

With dV/dt expressed in volts per minute the rate of ion pair production is

$$\frac{\text{ion pairs}}{\text{minute}} = \frac{C}{e} \frac{dV}{dt} \quad (3)$$

Since

$$W = \frac{\text{energy expended}}{\text{ion pairs produced}} \quad (4)$$

then

$$W = \frac{N E e}{C (dV/dt)} \quad (5)$$

and since e , E , C , and N were constant throughout the experiment,

$$W = \frac{k}{dV/dt} \quad (6)$$

or

$$\frac{dV}{dt} = \frac{k}{W} \quad (7)$$

Since in this study only relative W 's were needed it was much more convenient to compare the dV/dt values, in millivolts per minute. Curves were obtained showing the rate of change of charge on the capacitor versus the gas pressure. The argon data were compared, point for point, to the mixture data and the relative changes due to the impurities were calculated. The final data for argon and for each mixture are the averages of three separate determinations in each case.

In preparation for the spectrographic investigation the gas exposure chamber was connected to the gas system, pumped down, flushed three times with pure argon, pumped down again, and then opened to the ionization chamber. The gases, either pure argon or mixtures, were admitted to the ionization chamber in the manner previously described.

The exposure chamber was sealed at 750 mm of Hg and disconnected. It was then placed in a holder on the optical bench of the spectrograph. All exposures were made from the same holder and chamber position. The spark source was connected by cables to the exposure chamber electrode holders and operated for an automatically timed ten seconds. Without moving the film holder, the exposure chamber was removed, refilled and replaced, and another exposure was made. Three exposures were made on each film, one of pure argon and two separate mixings of the argon-impurity mixture. Each exposure used a band of film 2 mm wide. On a few films an additional band was exposed to a Hg vapor discharge tube.

The films were developed for three minutes in Kodak D-19 developer, placed in Kodak stop bath SB-5 for one minute, transferred to Kodak fixer F-5 for fifteen minutes, washed in cool running water for ten minutes, run through a Kodak Photo-Flo bath for thirty seconds, and then hung up to dry.

After drying, films were placed between two glass plates on the microphotometer film carriage. The microphotometer was then used to make a graphic representation on a paper tape of the density of the spectral lines on the film. The Hg spectrum was added to the film to be used as a standard, as Hg has a relatively simple and easily identifiable emission spectrum.⁴ The argon lines were identified by comparison with

4 Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland (1957-1958).

the Handbook values for Hg and by interpolation.

Each tape which represented the spectrum of a gas mixture was compared to the tape which represented the pure argon spectrum from the same film. This procedure eliminated errors which could be caused by slight variation in developing, placing of the film in the film carriage and focussing the microphotometer lenses. The tapes for the mixtures were compared, line by line, to the tapes for pure argon. Lines for which the film density was greatly reduced by the addition of the impurity were identified by wave length, and the electron transitions by which the argon atom emits these lines were determined.^{5,6} The atomic energy level at the start of each transition was then determined.⁷ To convert these levels into electron volts, the following method was used:

- h - 6.624×10^{-27} erg sec, Planck's constant;
- c - 2.99776×10^{10} cm/sec, speed of light in vacuo;
- ν - frequency, in sec^{-1} ;
- $\bar{\nu}$ - wave number, in cm^{-1} ;
- λ - wave length, in cm;
- E - energy, in ergs.

5 K. W. Meissner, Zeit. Phys. 39, 172 (1926); 40, 839 (1927).

6 J. B. Green and B. Fried, Phys. Rev. 54, 876 (1938).

7 Atomic Energy Levels, Circular 467, U. S. Dept. of Commerce, National Bureau of Standards (1949).

From the relationships,

$$\nu = \frac{c}{\lambda} \quad (8)$$

and

$$\bar{\nu} = \frac{1}{\lambda} \quad (9)$$

$$\nu = \bar{\nu} c \quad (10)$$

as

$$E = h\nu \quad (11)$$

Then

$$E = \bar{\nu} ch \quad (12)$$

This gives the energy in ergs. Dividing E by 1.602×10^{-12} ergs/ev converts energy to electron volts. The wave number is the difference between the atomic energy level at the start and at the end of the transition.

IV. DATA

Data from the Ionization Study

The ionization as a function of absolute pressure was measured three times for each of the gases used. These gases included: 97% argon-3% ethane; 99% argon-1% ethane; 97% argon-3% propane; 97% argon-3% nitrogen; 99.5% argon-0.5% acetylene; and pure argon. The ion current values for the three determinations at each pressure were averaged (Table I). The maximum deviations from the average values were as follows: for the argon-propane and the 97% argon-3% ethane mixtures, 0.75%; for the 99% argon-1% ethane mixture, 0.6%; for the argon-nitrogen and argon-acetylene mixtures, 0.5%; and for pure argon, 1.7%. The average value for each mixture was then compared to the average value for pure argon for each pressure and the percentage of difference was calculated (Table II). For the 97% argon-3% ethane, the 99% argon-1% ethane, and the 97% argon-3% propane mixtures, ionization versus pressure curves (Figs. 6,7,8) are similar in shape to the pure argon curve with which each is plotted. The argon-nitrogen data (Fig. 9) show no increase of ionization, as was expected.² The argon-acetylene curve (Fig. 10) is slightly different because the ionization current starts to decrease at a slightly higher pressure than for any other mixture or gas used. It should be noted that the ionization potential of propane (11.2 eV)² is well below; the ionization potential of acetylene (11.45 eV)² is slightly below; and the ionization potential of ethane (12.8 eV)⁴ is well above the metastable level of argon (11.5 eV). The ionization potential of molecular nitrogen

Table I

Average Ion Current Measured as Rate of Charging a Capacitor Versus Pressure for Several Gases

Pressure mm Hg	Pure Argon mv/min	97% Argon 3% Ethane mv/min	99% Argon 1% Ethane mv/min	97% Argon 3% Propane mv/min	99.5% Argon 0.5% Acetylene mv/min	97% Argon 3% Nitrogen mv/min
750	929.08 ± 1.95	993.71 ± 2.48	966.30 ± 2.42	1017.41 ± 2.54	1182.20 ± 10.52	922.74 ± 2.31
700	929.28 ± 1.95	995.82 ± 2.49	981.89 ± 2.45	1017.20 ± 2.54	1178.48 ± 10.49	918.47 ± 2.30
600	930.52 ± 1.95	997.90 ± 2.49	985.12 ± 2.46	1019.03 ± 2.55	1185.49 ± 10.35	914.75 ± 2.29
500	930.62 ± 1.95	999.11 ± 2.50	987.72 ± 2.47	1018.92 ± 2.55	1183.77 ± 10.54	915.84 ± 2.29
400	934.39 ± 1.96	996.60 ± 2.49	983.07 ± 2.46	1019.72 ± 2.55	1172.67 ± 10.44	917.16 ± 2.29
375	934.59 ± 1.96	993.71 ± 2.48	980.08 ± 2.45	1016.73 ± 2.54	1159.07 ± 10.32	915.77 ± 2.29
350	932.64 ± 1.96	999.69 ± 2.49	985.88 ± 2.46	1016.15 ± 2.54	1155.66 ± 10.29	913.71 ± 2.28
325	927.74 ± 1.95	994.27 ± 2.49	977.30 ± 2.44	1011.15 ± 2.53	1142.48 ± 10.17	912.23 ± 2.28
300	913.34 ± 3.01	980.40 ± 3.63	969.20 ± 3.59	994.50 ± 3.68	1126.17 ± 11.37	900.37 ± 3.33
275	891.71 ± 2.94	962.27 ± 3.56	946.18 ± 3.50	978.92 ± 3.62	1093.09 ± 11.04	875.06 ± 3.24
250	856.37 ± 2.83	931.24 ± 3.45	912.60 ± 3.38	994.21 ± 3.49	1049.05 ± 10.60	841.52 ± 3.11

Table I (continued)

Average Ion Current Measured as Rate of Charging a Capacitor Versus Pressure for Several Gases

Pressure mm Hg	Pure Argon mv/min	97% Argon 3% Ethane mv/min	99% Argon 1% Ethane mv/min	97% Argon 3% Propane mv/min	99.5% Argon 0.5% Acetylene mv/min	97% Argon 3% Nitrogen mv/min
225	784.31 ± 2.59	873.96 ± 3.23	850.82 ± 3.15	879.43 ± 3.25	969.10 ± 9.79	772.67 ± 2.86
200	675.78 ± 2.16	769.37 ± 2.77	747.63 ± 2.69	764.47 ± 2.75	827.36 ± 8.27	665.44 ± 2.40
175	578.97 ± 1.85	633.45 ± 2.28	614.26 ± 2.21	649.37 ± 2.34	710.74 ± 7.11	571.19 ± 2.06
150	477.08 ± 1.52	518.49 ± 1.87	503.25 ± 1.81	531.42 ± 1.91	582.27 ± 5.82	467.16 ± 1.68
125	385.57 ± 1.23	414.25 ± 1.49	402.83 ± 1.45	429.92 ± 1.55	467.20 ± 4.67	383.66 ± 1.38
100	300.66 ± 1.47	319.02 ± 1.69	306.57 ± 1.62	335.04 ± 1.78	362.83 ± 4.25	295.16 ± 1.56
75	218.23 ± 1.07	235.19 ± 1.25	227.89 ± 1.21	241.50 ± 1.28	262.55 ± 3.07	214.41 ± 1.14
50	143.49 ± 0.70	152.15 ± 0.81	148.56 ± 0.79	157.30 ± 0.83	173.68 ± 2.03	140.76 ± 0.75
25	70.61 ± 0.35	74.74 ± 0.40	73.08 ± 0.39	77.86 ± 0.41	85.76 ± 1.00	71.34 ± 0.38
15	44.53 ± 0.22		45.14 ± 0.24	48.76 ± 0.26	52.73 ± 0.62	44.39 ± 0.24
10	29.56 ± 0.14		30.06 ± 0.16	32.43 ± 0.17	35.28 ± 0.41	28.99 ± 0.15

Table II

Ionization of Argon-Impurity Mixtures Expressed as Per Cent Higher
than Ionization of Pure Argon (Per Cent Lower for Nitrogen)

Pressure mm Hg	97% Argon 3% Ethane	99% Argon 1% Ethane	97% Argon 3% Propane	99.5% Argon 0.5% Acetylene	97% Argon 3% Nitrogen
750	6.956 \pm 0.493	4.006 \pm 0.479	9.561 \pm 0.503	27.244 \pm 1.399	0.682 \pm 0.460
700	7.160 \pm 0.494	5.661 \pm 0.485	9.461 \pm 0.503	26.816 \pm 1.395	1.164 \pm 0.460
600	7.240 \pm 0.493	5.867 \pm 0.486	9.511 \pm 0.504	27.309 \pm 1.375	1.696 \pm 0.459
500	7.360 \pm 0.494	6.136 \pm 0.488	9.488 \pm 0.503	27.202 \pm 1.399	1.588 \pm 0.459
400	6.658 \pm 0.491	5.210 \pm 0.484	9.132 \pm 0.502	25.501 \pm 1.381	1.844 \pm 0.459
375	6.326 \pm 0.489	4.867 \pm 0.482	8.789 \pm 0.500	24.019 \pm 1.364	2.014 \pm 0.459
350	6.868 \pm 0.492	5.709 \pm 0.486	8.954 \pm 0.501	23.913 \pm 1.364	2.021 \pm 0.457
325	7.170 \pm 0.496	5.342 \pm 0.484	8.991 \pm 0.502	23.147 \pm 1.355	1.672 \pm 0.460
300	7.342 \pm 0.754	6.116 \pm 0.743	8.886 \pm 0.762	23.302 \pm 1.651	1.420 \pm 0.699
275	7.913 \pm 0.757	6.108 \pm 0.742	9.780 \pm 0.768	22.584 \pm 1.642	1.867 \pm 0.699
250	8.743 \pm 0.776	6.566 \pm 0.747	10.024 \pm 0.771	22.383 \pm 1.634	1.734 \pm 0.699

Table II (continued)

Ionization of Argon-Impurity Mixtures Expressed as Per Cent Higher
than Ionization of Pure Argon (Per Cent Lower for Nitrogen)

Pressure	97% Argon 3% Ethane	99% Argon 1% Ethane	97% Argon 3% Propane	99.5% Argon 0.5% Acetylene	97% Argon 3% Nitrogen
225	11.430 ± 0.783	8.480 ± 0.760	12.128 ± 0.785	23.561 ± 1.656	1.484 ± 0.700
200	13.849 ± 0.776	10.632 ± 0.752	13.124 ± 0.769	22.430 ± 1.615	1.530 ± 0.620
175	9.410 ± 0.746	6.095 ± 0.721	12.160 ± 0.763	22.759 ± 1.620	1.344 ± 0.733
150	8.680 ± 0.740	6.787 ± 0.885	11.390 ± 0.755	22.049 ± 1.609	2.079 ± 0.677
125	7.438 ± 0.732	4.476 ± 0.709	11.502 ± 0.746	21.171 ± 1.598	0.495 ± 0.678
100	6.107 ± 1.086	1.966 ± 1.038	11.435 ± 1.137	21.010 ± 2.005	1.820 ± 1.012
75	7.772 ± 1.106	4.427 ± 1.067	10.663 ± 1.129	20.309 ± 1.997	1.750 ± 1.021
50	6.035 ± 1.087	3.533 ± 1.056	9.624 ± 1.113	21.046 ± 2.006	1.903 ± 1.020
25	5.849 ± 1.097	3.498 ± 1.065	10.268 ± 1.127	21.456 ± 2.018	-0.103 ± 0.104
15		3.699 ± 2.808	9.499 ± 1.125	18.415 ± 1.977	0.314 ± 1.033
10		1.691 ± 1.023	9.709 ± 1.095	19.350 ± 1.952	1.928 ± 0.990

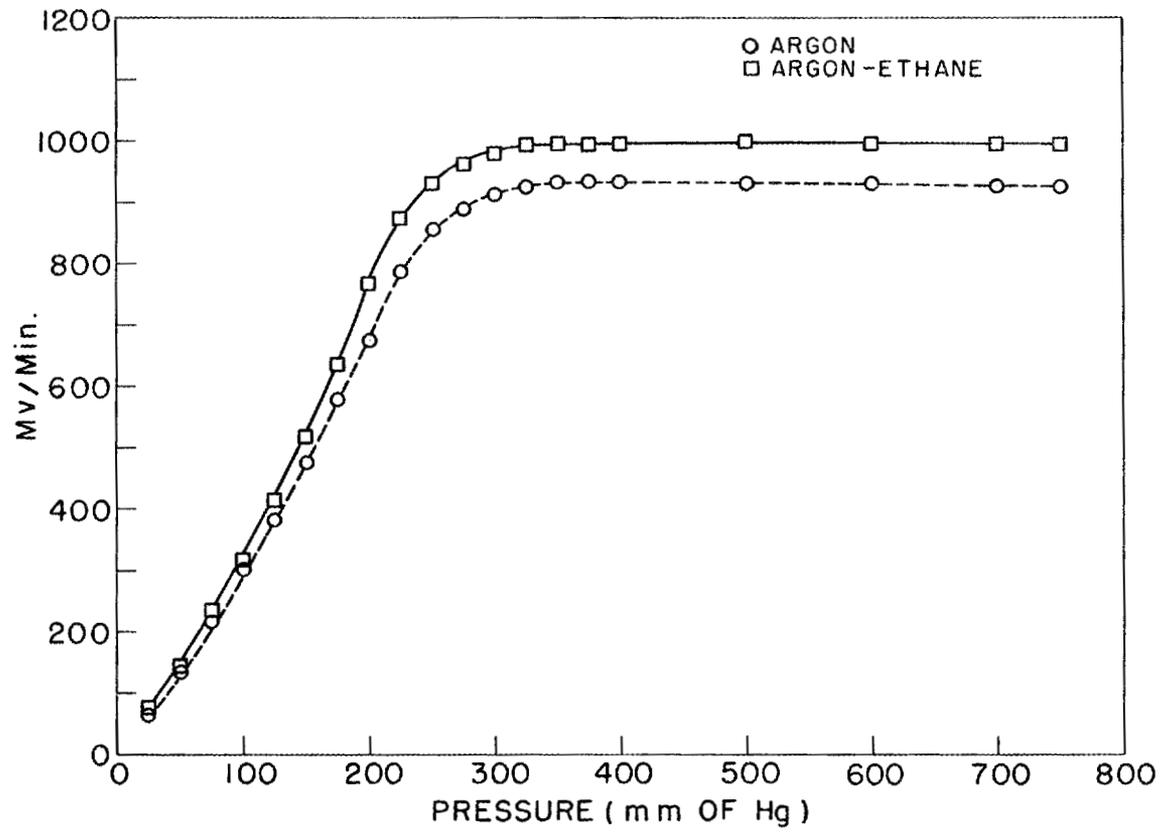
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FIG. 6. IONIZATION VERSUS PRESSURE OF ARGON AND 97% ARGON-3% ETHANE MIXTURE

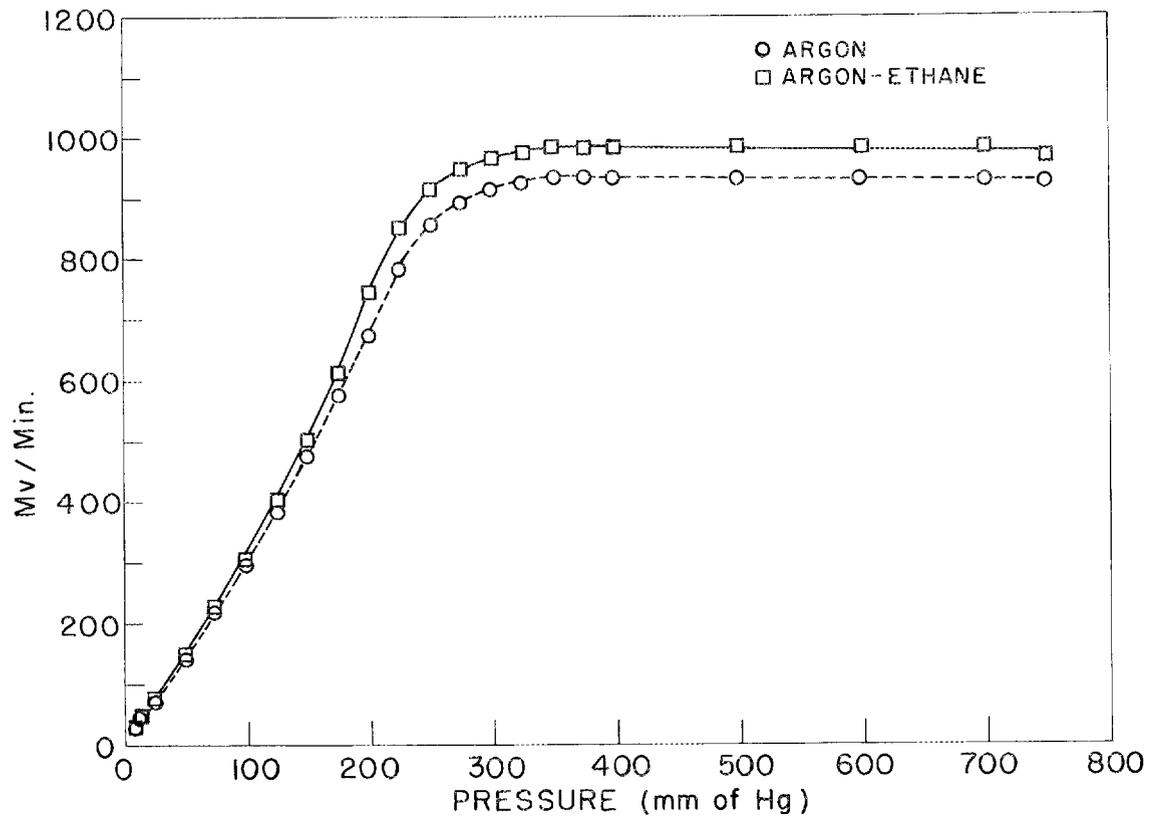
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FIG. 7. IONIZATION VERSUS PRESSURE OF ARGON AND 99% ARGON-1% ETHANE MIXTURE

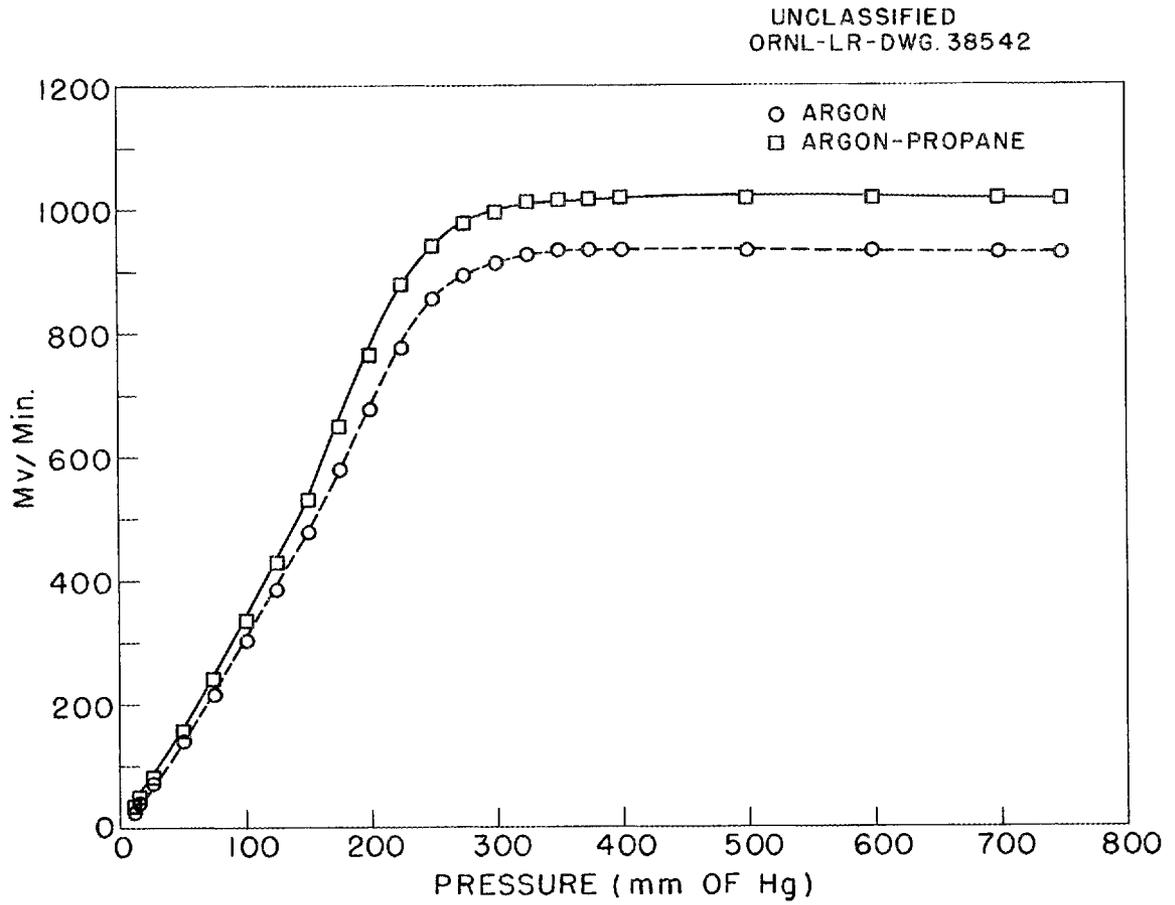


FIG. 8. IONIZATION VERSUS PRESSURE OF ARGON AND 97% ARGON-3% PROPANE MIXTURE

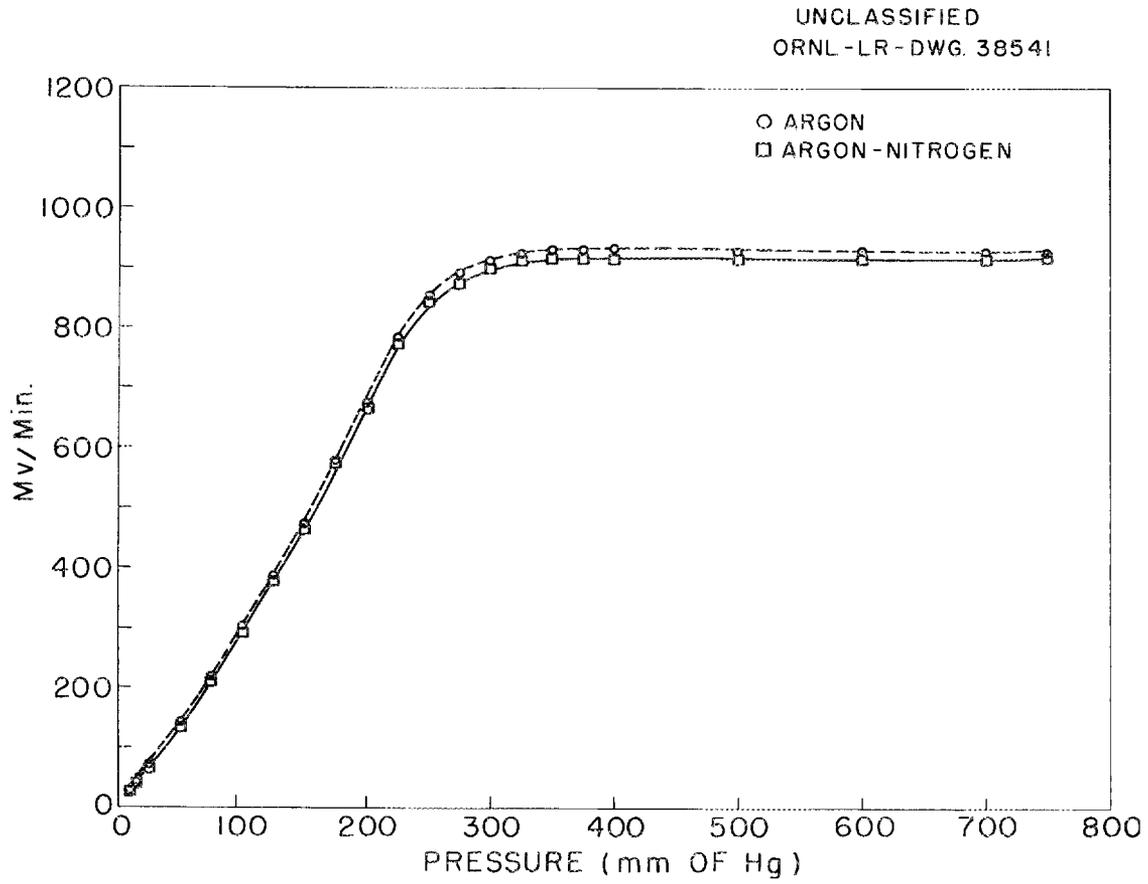


FIG. 9. IONIZATION VERSUS PRESSURE OF ARGON AND 97% ARGON-3% NITROGEN MIXTURE

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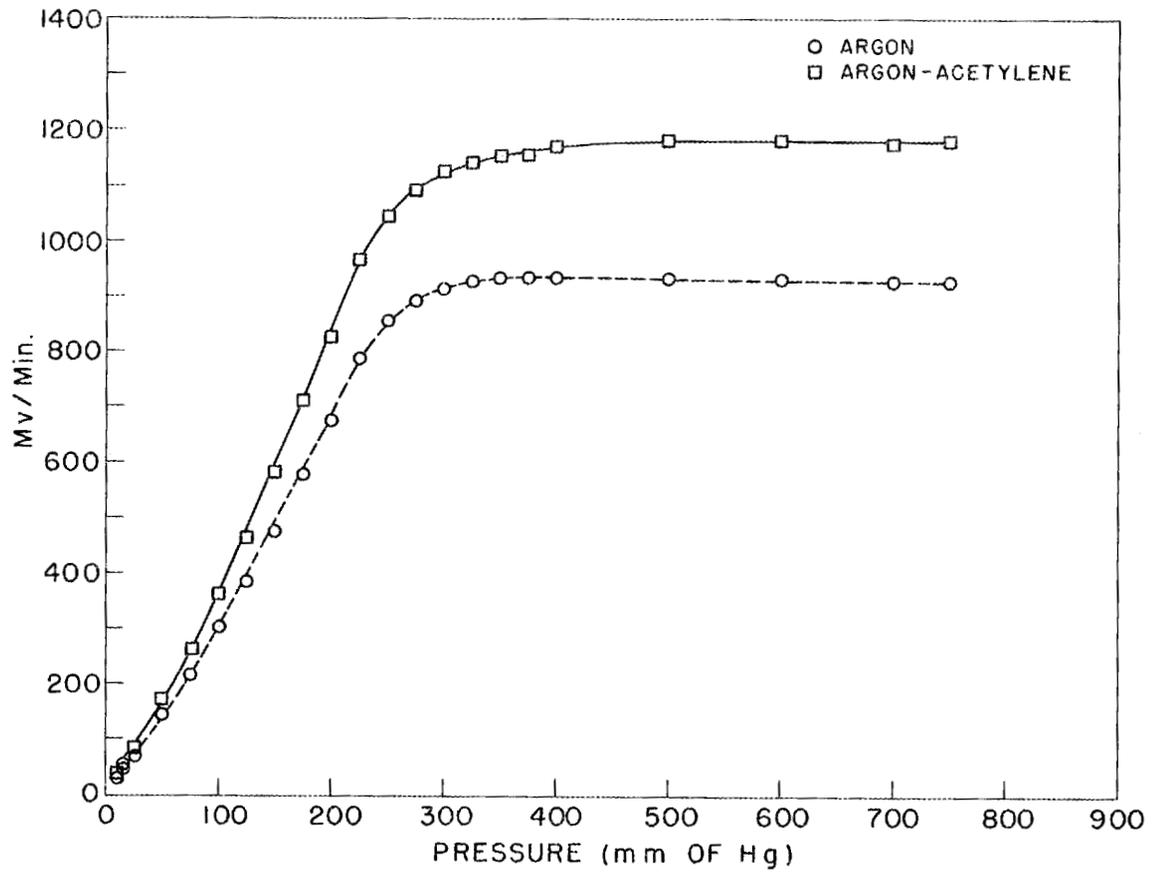


FIG. 10. IONIZATION VERSUS PRESSURE OF ARGON AND 99.5% ARGON-.5% ACETYLENE MIXTURE

(15.51 ev) is above that of ethane.

Differentiating the curve in Fig. 6 with respect to pressure (Fig. 11) shows the similarity of curve shape for pure argon and the argon-ethane mixture since differential curves emphasize differences in the slopes of integral curves. This similarity of shape is maintained as the pressure is lowered until the range of the alpha particles equals the distance to the boundary of the sensitive volume of the ionization chamber. This pressure is slightly lower for the argon-ethane mixture than for pure argon because the mass stopping power of ethane is greater than that of argon. The similarity of the shapes of the ionization versus pressure curves shows that the magnitude of the increased ionization effect is not dependent on total pressure.

The errors introduced by starting and stopping the stop watch which was used to measure the time required to charge the capacitor were less than $\pm 0.21\%$, and the errors in the percentage of impurity were not greater than $\pm 0.08\%$. Errors were most significant in the argon-acetylene mixture in which W changes the most rapidly as a function of percentage of impurity.² The maximum errors introduced by variations in mixing were $\pm 0.68\%$ for the argon-acetylene mixture and $\pm 0.04\%$ for the other mixtures. Deviations in filling pressure were most important at pressures below that at which the range of the alpha particles is equal to the shortest path from the alpha source to the boundary of the sensitive volume of the ionization chamber. The absolute error in reading a pressure gauge remains constant throughout its range, however

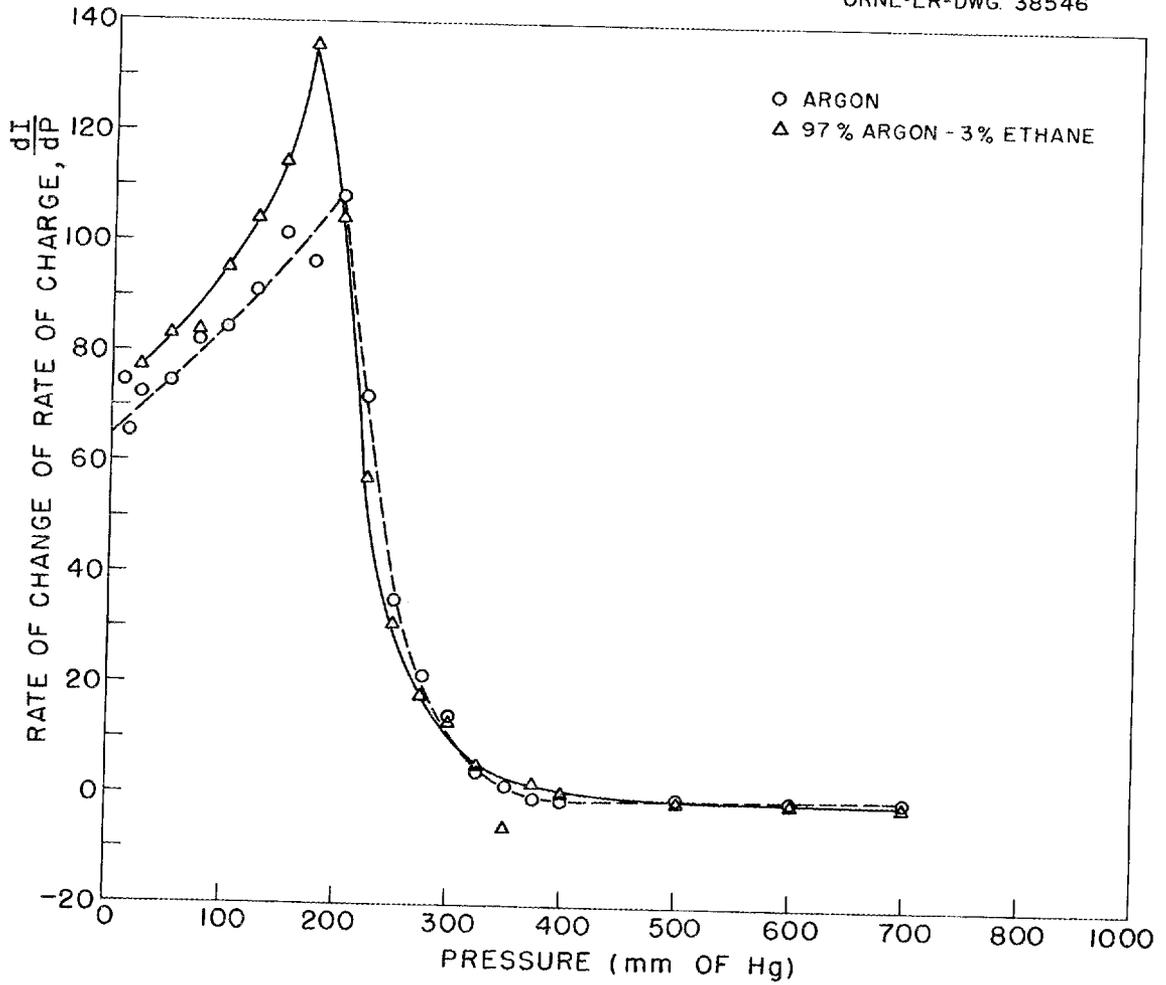
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FIG. 11. RATE OF CHANGE OF RATE OF CHARGE VERSUS PRESSURE FOR ARGON AND 97% ARGON-3% ETHANE MIXTURE

the relative error changes as a function of pressure. For convenience the gas pressures used were divided into four ranges and a maximum relative error was calculated for each range. Total errors are shown in Table III.

Data from the Spectrum Study

In the spectrographic study, ethane was the impurity of principal concern because its ionization potential lies above the metastable level of argon and below the 14.5 to 15.5 eV energy level range under consideration. For this reason the argon-ethane data were of greater interest than those for other impurities.

A comparison of the microphotometer tapes for pure argon and 97% argon-3% ethane mixture showed a significant reduction in the film densities for some of the spectral lines of argon in the mixture. This reduction, due to the addition of the ethane, ranged from 0.0 to 0.7. Several lines were of exactly the same density as for pure argon. Table IV lists the effect of the ethane addition on thirty-eight lines.

A comparison of the argon-nitrogen spectrum with the pure argon spectrum showed no significant reduction of any of the argon lines. There were, however, nitrogen lines added to the spectrum. The argon-propane and argon-acetylene spectra showed a general reduction of intensity for all argon lines. The ionization potentials of both acetylene and propane are lower than the lowest excitation potential of argon. Therefore, the addition of acetylene or propane should decrease the intensity of all argon lines.

Table III
Total Relative Error of Data for Various Gases and Pressures

Gas	Pressure in mm of Hg			
	$p > 300$	$300 > p > 200$	$200 > p > 100$	$100 > p > 0$
Argon	0.21%	0.33%	0.32%	0.49%
Argon-Ethane	0.25%	0.37%	0.36%	0.53%
Argon-Propane	0.25%	0.37%	0.36%	0.53%
Argon-Ni trogen	0.25%	0.37%	0.36%	0.53%
Argon-Acetylene	0.89%	1.01%	1.00%	1.17%

Table IV

Effect on the Film Density of Several Lines of the Emission Spectrum of Argon by the Addition of 3% Ethane

Wave Length (\AA)	Transition	Upper Energy Level (cm^{-1})	Upper Energy Level (ev)
<u>Reduction to 0.3</u>			
5698.64	$2p_6 - 6d_3$	123808.60	15.366
5581.83	$2p_9 - 5s_1^{11}$	123372.987	15.311
5073.08	$2p_{10} - 5s_1^1$	123815.53	15.366
5062.72	$2p_6 - 9s_4$	125984.35	15.636
5032.02	$2p_9 - 7s_5$	125329.99	15.554
5017.25	$2p_6 - 11d_1^1$	126163.24	15.658
4804.33	$2p_8 - 13d_4$	126426.07	15.690
4798.74	$2p_9 - 12d_4^1$	126295.79	15.674
<u>Reduction to 0.4</u>			
5118.20	$2p_8 - 6s_1^{111}$	125150.00	15.532
5048.81	$2p_{10} - 5s_5$	123903.295	15.377
4846.73	$2p_9 - 7s_1^{111}$	126089.56	15.649
4768.67	$2p_{10} - 6s_1^{11}$	125066.501	15.522
3606.52	$1s_4 - 4p_5$	121470.304	15.117

Table IV (continued)

Effect on the Film Density of Several Lines of the Emission
Spectrum of Argon by the Addition of 3% Ethane

Wave Length (\AA)	Transition	Upper Energy Level (cm^{-1})	Upper Energy Level (ev)
<u>Reduction to 0.5</u>			
6307.66	$2p_6 - 5d_3$	122086.974	15.152
5882.08	$2p_{10} - 3s_3$	121096.67	15.029
3783.52	$2p_7 - 5s_1^{11}$	123372.987	15.311
5774.00	$2p_3 - 7d_3$	124603.957	15.464
5700.86	$2p_6 - 6d_4$	123773.920	15.361
5506.11	$2p_8 - 6d_4$	123773.920	15.361
5241.10	$2p_8 - 7d_1^{11}$	124692.02	15.475
5219.30	$2p_8 - 6s_5$	124771.67	15.485
4969.88	$2p_7 - 6s_3$	126202.82	15.663
4956.75	$2p_9 - 9d_4^1$	125631.69	15.592
4589.29	$1s_2 - 3p_6$	117183.654	14.543
3398.75	$\left\{ \begin{array}{l} 1s_2 - 7x \\ 1s_5 - 5p_4 \end{array} \right\}$	124857.27	15.495
		124643.54	15.587
<u>Reduction to 0.7</u>			
3670.64	$1s_2 - 4p_3$	122635.128	15.20
3563.26	$1s_3 - 4p_2$	122601.290	15.20

Table IV (continued)

Effect on the Film Density of Several Lines of the Emission
Spectrum of Argon by the Addition of 3% Ethane

Wave Length (\AA°)	Transition	Upper Energy Level (cm^{-1})	Upper Energy Level (ev)
<u>Reduction to 0.9</u>			
7107.496	$2p_8 - 3s_5$	119683.113	14.83
6105.639	$2p_4 - 5s_1^{111}$	123505.536	15.31
6145.43	$2p_3 - 5s_1^{111}$	123557.459	15.32
6155.23	$\left\{ \begin{array}{l} 2p_6 - 4s_4 \\ 2p_4 - 5s_1^{11} \end{array} \right\}$	122479.459	15.18
		123372.987	15.29
6098.807	$2p_7 - 4s_4$	122479.459	15.18
<u>No Reduction</u>			
3632.684	$1s_4 - 4p_6$	121270.682	15.03
3559.3061	$1s_5 - 4p_6$	121270.682	15.03
3567.6565	$1s_5 - 4p_2$	121165.431	15.02
7206.986	$2p_3 - 3s_2$	121161.356	15.02
6170.183	$2p_6 - 4s_5$	122440.109	15.18
3635.54	$2p_7 - 6d_1^{11}$	123826.85	15.35

For all gas mixtures the film densities were repeated very accurately by a second determination.

V. DISCUSSION

The increase of ionization due to the addition of an impurity to argon might be explained by the existence of a metastable state in argon at an energy level between 14.5 and 15.5 eV, the energy range in which the increased ionization effect disappears. Electrons in a metastable level can be released in the following ways: (a) the energy might be used in the ionization by collision of another gas; (b) the collision of two metastable atoms might produce an ion pair; (c) the metastable atom or molecule might be excited to a higher level and radiate a photon; (d) it might diffuse to the walls of the container; or (e) an electron transition accompanied by the emission of a photon might occur. Process (a) would contribute to the increase of ionization by the addition of a proper impurity. Processes (b), (c), (d), and (e) would be affected little, if at all, by the impurity addition. However, there are no excited levels of atomic argon above the known metastable levels for which the selection rules prohibit optical transitions.⁷ There are, therefore, no metastable excited states of atomic argon in the energy range under consideration. The constancy of the relative ion current during large pressure changes indicates that metastable argon molecules do not contribute to the increased ionization for argon-impurity mixtures because the concentration of molecular argon would be pressure dependent. Therefore, the mechanism must not depend upon an additional metastable level, atomic or molecular.

The suggestion that the additional ionization effect is due to ionization of the impurity by subexcitation electrons was examined in the following manner: subexcitation electrons in argon by definition must have kinetic energies less than 11.5 eV, the lowest excited level of argon. According to theory, these electrons would be capable of ionizing impurities whose ionization potentials were equal to or less than the energy of the electrons. The increased ionization effect has been shown to take place due to the addition of impurities with ionization potentials ranging up to 14.5 eV. Therefore, the effect could not be due to subexcitation electrons alone.

The number of ions formed in a gas by electrons depends on the number of electrons which have energy equal to or exceeding the ionization potential of the gas. In an ionization chamber the energy distribution of electrons is a function of E/P. The energy of the peak population is altered by changing E/P, and the whole energy distribution is shifted correspondingly. The mean energy, ϵ , of the population can be calculated⁸ by the formula,

$$\epsilon = 0.04 \times k \quad (13)$$

where k , the mean energy of agitation of an electron in terms of the mean energy of agitation of a molecule of argon at 15° C, is a function of E/P and is tabulated from experimental data. Increasing E/P from 0.00948 to

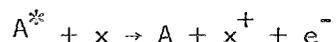
⁸ J. S. Townsend and V. A. Bailey, Phil. Mag. 44, 1033 (1922).

0.718 ($k = 67$ to 241 , respectively) would shift ϵ from 2.68 eV to 9.64 eV. This would not shift the mean energy of the population to an energy greater than the ionization potential of ethane (12.8 v), but it would definitely increase the number of electrons with sufficient energy to ionize ethane

If electrons were contributing significantly to the added ionization a shift of E/P through this range would have caused marked changes in the total amount of ionization, but the total ionization remained constant through this range of E/P . Therefore, agitation electrons, like sub-excitation electrons, cannot contribute significantly to the extra ionization effect.

A relatively long lived excited state which is not metastable would have the same possibilities for loss of energy as a metastable state. The increased ionization effect studied was shown to be pressure independent but impurity dependent. Processes (b) and (d) would be independent of the presence of impurities and would be pressure dependent. Process (e) in itself would be impurity and pressure independent but might accompany processes (a) and (c).

If we consider process (a),

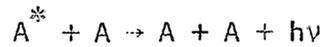


the rate at which long lived excited argon atoms, A^* , would be discharged would depend on some constant, C_1 , on the pressure of the impurity, P_x ,

and on the number of long lived excited argon atoms present, N .

$$\left(\frac{dN}{dt}\right)_1 = -C_1 P_x N \quad (14)$$

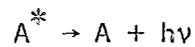
Similarly, for process (c),



the rate of excited argon discharge depends on some constant, C_2 , the pressure of argon, P_a , and on the number of long lived excited argon atoms present.

$$\left(\frac{dN}{dt}\right)_2 = -C_2 P_a N \quad (15)$$

Process (e),



would depend only on the decay constant of the excited argon atoms, λ , and on the number of long lived excited argon atoms present, N .

$$\left(\frac{dN}{dt}\right)_3 = -\lambda N \quad (16)$$

For these processes,

$$\frac{dN}{dt} = \left(\frac{dN}{dt}\right)_1 + \left(\frac{dN}{dt}\right)_2 + \left(\frac{dN}{dt}\right)_3 \quad (17)$$

Substituting from Eqs. (14), (15), and (16),

$$\frac{dN}{dt} = -C_1 P_x N - C_2 P_a N - \lambda N \quad (18)$$

On rearranging,

$$\frac{dN}{N} = - \left(C_1 P_x + C_2 P_a + \lambda \right) dt \quad (19)$$

Integrating both sides gives

$$\ln N = - \left(C_1 P_x + C_2 P_a + \lambda \right) t + k \quad (20)$$

where k is a constant of integration.

$$N = N_0 e^{-(C_1 P_x + C_2 P_a + \lambda) t} \quad (21)$$

where N_0 , a constant, is the number of long lived excited argon atoms at time = 0.

Substituting into Eq. (14) gives

$$\left(\frac{dN}{dt} \right)_1 = - C_1 P_x N_0 e^{-(C_1 P_x + C_2 P_a + \lambda) t} \quad (22)$$

or

$$dN_1 = - C_1 P_x N_0 e^{-(C_1 P_x + C_2 P_a + \lambda) t} dt \quad (23)$$

Integrating both sides,

$$N_1 = - C_1 P_x N_0 \int_0^{\infty} e^{-(C_1 P_x + C_2 P_a + \lambda)t} dt \quad (24)$$

Evaluating the integral,

$$N_1 = \frac{C_1 P_x}{C_1 P_x + C_2 P_a + \lambda} N_0 \quad (25)$$

Since total pressure, P , is the sum of the partial pressures,

$$P = P_x + P_a \quad (26)$$

the partial pressure may be considered to be a certain fraction, f , of the total pressure,

$$P_x = f_1 P \quad (27)$$

$$P_a = f_2 P \quad (28)$$

Substituting in Eq. (25),

$$N_1 = \frac{C_1 f_1 P}{C_1 f_1 P + C_2 f_2 P + \lambda} N_0 = \frac{P C_1 f_1}{P(C_1 f_1 + C_2 f_2 + \lambda/P)} N_0 = \frac{C_1 f_1}{C_1 f_1 + C_2 f_2 + \lambda/P} N_0 \quad (29)$$

It is thus seen that a competition between ionizing collisions with impurities and photon emission following argon-argon collisions can exist which, except for the term λ/P in the denominator, is not dependent upon total pressure, but only upon the percentage of impurity present. During the course of ionization chamber experiments, ionization was found to remain constant while composition of the gas mixture was held constant and total pressure was varied.

Since experimental results require ionization to be independent of pressure, λ/P will be assumed to be small compared to $C_1 f_1 + C_2 f_2$. This assumption will be examined later. Equation (29) can now be written

$$N_1 = \frac{C_1 f_1}{C_1 f_1 + C_2 f_2} N_0 \quad (30)$$

Bortner and Hurst⁹ have shown that a formula for the value of W of gas mixtures may be written as follows,

$$\frac{1}{W_m} = \left(\frac{1}{W_1} - \frac{1}{W_2} \right) z + \frac{1}{W_2} \quad (31)$$

where

$$z = \frac{P_1}{P_1 + a_{12} P_2} \quad (32)$$

9 T. E. Bortner and G. S. Hurst, Phys. Rev. 93, 1236 (1954).

and a_{12} is an empirical constant.

If, as before we let

$$f_1 P = P_1 \quad (33)$$

and

$$f_2 P = P_2 \quad (34)$$

then

$$z = \frac{f_1}{f_1 + a_{12} f_2} \quad (35)$$

Thus z is not dependent on pressure but upon composition of the mixture. If this formula were applied to an argon-impurity mixture, it would fail because the one component of the mixture contributes to the ionization of the other. It is necessary to add a correction to account for the extra ionization of the impurity by the excited argon. From Eq. (30), N_1 , the number of long lived excited argon atoms which will undergo process (a), $A^* + x \rightarrow A + x^+ + e^-$, is

$$N_1 = N_0 \frac{c_1 f_1}{c_1 f_1 + c_2 f_2}$$

This can be rewritten as

$$N_1 = N_0 \frac{f_1}{f_1 + (c_2/c_1) f_2} \quad (36)$$

Set

$$\frac{f_1}{f_1 + (C_2/C_1)f_2} = Y \quad (37)$$

and let α be a quantity proportional to N_0 . The term αY was selected to be added to Eq. (31) for the following reasons:

- 1) the magnitude of the extra ionization effect must have a relationship to the number of excited argon atoms,
- 2) the effect must be independent of total pressure,
- 3) the correction term should allow the competition between ionization and collision induced photon emission, and
- 4) it is reasonable to assume that this correction term might have the same general form as z .

The addition of αY to Eq. (31) gives

$$\frac{1}{W_m} = \left(\frac{1}{W_1} - \frac{1}{W_2} \right) z + \frac{1}{W_2} + \alpha Y \quad (38)$$

This implies that the extra ionization would increase monotonically as f_1 , the fraction of impurity, increases to 1. This cannot be true, for, as f_1 increases, the number of argon atoms available to form the long lived excited atoms, A^* , would decrease to 0.

To account for the decrease in the availability of argon, the factor $(1 - z)$ was introduced. The factor $(1 - z)$ was selected because

the term z had already been used to describe the effect of the change of composition of the gas, and $(1 - z)$ goes to 0 as the fraction of argon goes to 0. The result is the corrected formula,

$$\frac{1}{W_m} = \left[\left(\frac{1}{W_1} - \frac{1}{W_2} \right) z + \frac{1}{W_2} \right] + \alpha Y (1 - z) \quad (39)$$

The solid line in Fig. 12 is a plot of Melton's data² for the value of W , for a mixture of argon and ethane, as a function of the composition of the gas. The broken line is a plot of W as a function of composition by use of Eq. (39). The values of $a_{12} = 2.13 \times 10^{-1}$, $(C_2/C_1) = 4.0 \times 10^{-3}$, and $\alpha = 4.1 \times 10^{-4}$ were chosen to give the best fit.

The maximum deviation of the calculated curve from the experimental curve is 0.8%. This is 0.3% greater than the probable experimental error. The accuracy of the value of W , calculated from this relatively simple formula, lends strong support to the theory of two competing processes, ionization versus photon emission.

The assumption that the term λ/P in Eq. (29) is not significant can now be examined more fully. If λ/P were much smaller than $C_1 f_1 + C_2 f_2$, the competition between ionization and photon emission following a collision would be independent of pressure. An equivalent condition is that in Eq. (25) λ is much smaller than $C_1 P_x + C_2 P_a$. A probable maximum value for $C_1 P_x + C_2 P_a$ can be calculated.

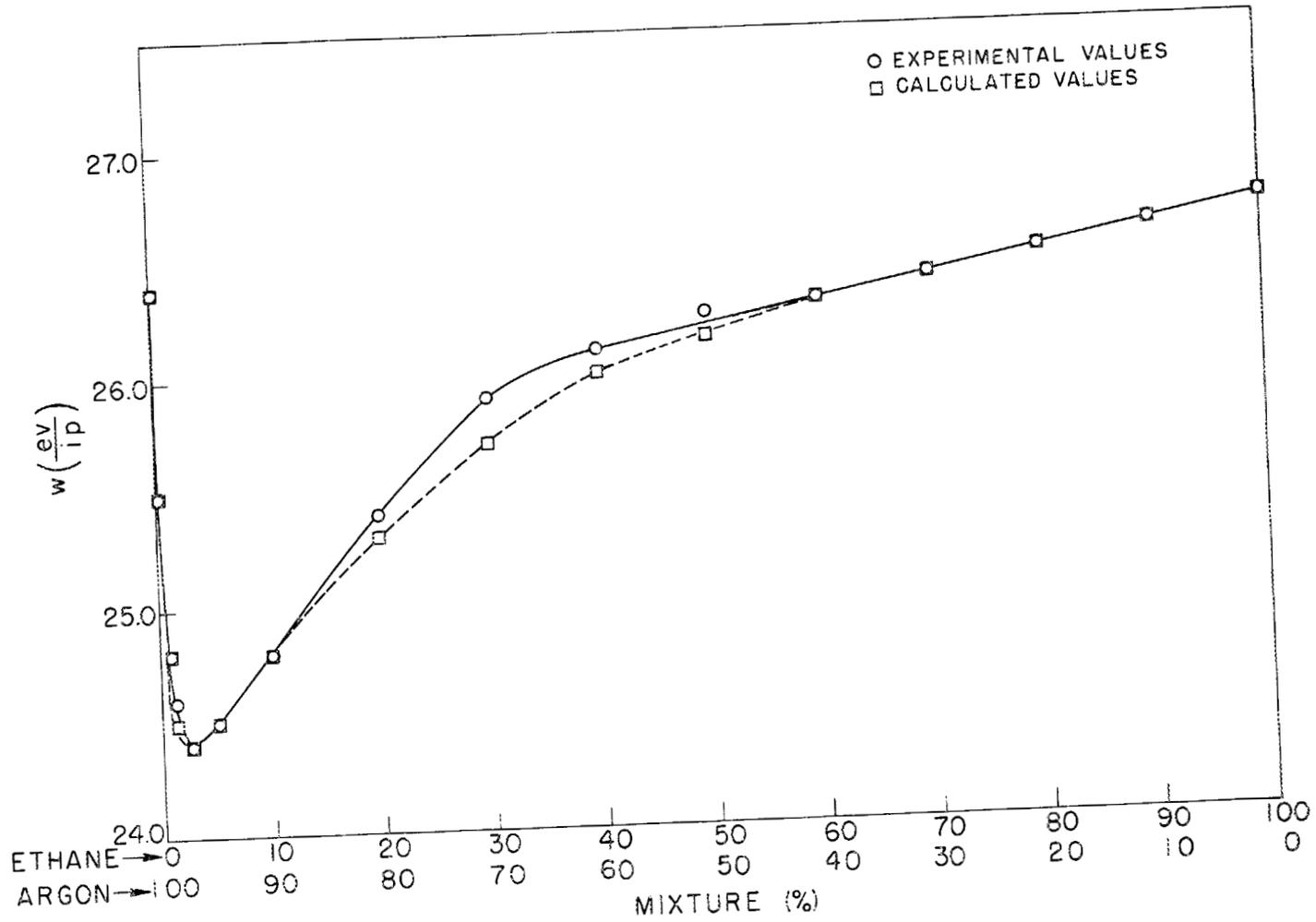


FIG. 12. CALCULATED AND EXPERIMENTAL VALUES OF W AS A FUNCTION OF GAS COMPOSITION

$$\left(\frac{dN}{dt}\right)_1 = -\sigma N \underline{n_x} \bar{v} \quad (40)$$

where

σ is the cross section for ionization in process (a) in cm^2 ,
 $\underline{n_x}$ is the number of molecules of impurity per cm^3 ,
 \bar{v} is the velocity of the molecules and atoms in cm sec^{-1} , and
 N is the number of excited argon atoms.

Using Eq. (14),

$$-C_1 P_x N = -\sigma N \underline{n_x} \bar{v} \quad (41)$$

or

$$C_1 P_x = \sigma \underline{n_x} \bar{v} \quad (42)$$

A maximum value for σ may be obtained by taking the gas kinetic cross section, i.e. about 10^{-16} cm^2 . The velocity, \bar{v} , is about $5 \times 10^4 \text{ cm sec}^{-1}$. In a mixture of 97% argon and 3% ethane, for example, with a total pressure of 750 mm Hg, $\underline{n_x}$ would equal $7.5 \times 10^{17} \text{ molecules cm}^{-3}$. From Eq. (42),

$$C_1 P_x = 3.75 \times 10^6 \text{ sec}^{-1} \quad (43)$$

Using the value 4.0×10^{-3} for the ratio C_2/C_1 obtained by the curve fitting procedures, the value of $C_2 P_a$ is seen to be

$$C_2 P_a = 4.86 \times 10^5 \text{ sec}^{-1} \quad (44)$$

$$C_1 P_x + C_2 P_a = 4.2 \times 10^6 \text{ sec}^{-1} \quad (45)$$

Therefore, if λ is much less than $4.2 \times 10^6 \text{ sec}^{-1}$, the natural lifetime of the excited state of argon,

$$\tau = 1/\lambda \quad (46)$$

is much greater than $2.4 \times 10^{-7} \text{ sec}$. If σ were as small as 10^{-18} cm^2 , τ would have to be greater than $2.4 \times 10^{-5} \text{ sec}$.

Such a range of values for the lifetime would not be unreasonable especially if imprisonment were to take place, i.e. the energy of excitation could be transferred by collision from one argon atom to another so that an argon atom in the excited state would exist although it would not be the identical argon atom. In this manner the energy causing the excited state would remain in argon for a longer time before dissipation. Meissner and Graffunder¹⁰ have reported half lifetimes of non-metastable excited argon atoms of up to 3.6×10^{-3} seconds.

If by the addition of an impurity, an increase in ionization takes place, it follows that a significant fraction of the excited argon atoms which, in pure argon, would return to ground state through optical

10 K. W. Meissner and W. Graffunder, Ann. Physik 84, 1009 (1927).

transitions will return to ground state through ionizing collisions with the impurity. The consideration of this implication leads to the examination of the emission spectrum of argon and the changes in it caused by the addition of impurities. There might be a group of lines in the spectrum of excited argon corresponding to the transitions starting from the proposed long lived state, process (e), and from levels slightly above the long lived state, process (c). Competition from another process, (a), brought about by the addition of an impurity to the argon would allow a smaller number of excited argon atoms to undergo the transitions in (c) and (e). Therefore, these spectral lines would be less intense in the presence of an impurity which could be ionized by argon atoms in a long lived excited state. There would, of course, be additional lines in the mixture spectrum due to excited atoms or molecules of the impurity.

The detection of 25 lines of the argon spectrum for which the film density was reduced to 0.5 or less by the addition of an impurity, ethane, is significant evidence of the existence of the proposed competition between ionization and optical transitions. Since this competition depends on an excited state of atomic argon with a lifetime long enough to permit ionizing collisions with impurity atoms or molecules, the reduced film density of the argon spectral lines strongly indicates the existence of such a state.

VI. CONCLUSION

The existence of one or more long lived non-metastable excited states of argon in the 15 to 15.5 ev range has been indicated. The increased ionization observed when certain impurities are added to argon is attributed to this long lived excited state rather than to molecular argon or subexcitation electrons. A competitive process between optical decay and ionizing collisions was evidenced by spectral analysis of the gas mixtures. From these experiments it was not possible to determine the exact energy levels of the suggested long lived excited states. Valuable additional information could be gained by performing a spectrographic study of the effects of the addition to argon of several impurities using alpha particles instead of electric sparks as a source of excitation. This study should include observation of lines in at least part of the ultraviolet region and in the infrared region as well as in the visible region.

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