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Energy Required to Produce One Ion Pair for Several Gases*

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The absolute values of W, the energy required to produce one ion pair, for electrons have been determined for several gases. A parallel plate extrapolation ionization chamber in conjunction with a ferrous sulfate dosimeter was used. The gases investigated were air, nitrogen, oxygen, carbon dioxide, argon, methane, and ethylene; and the absolute values of W were 33.9, 34.8, 30.9, 32.6, 25.5, 26.8, and 26.3 ev, respectively.

INTRODUCTION

IN a previous publication,[1] we have described an experimental determination of G, the oxidation yield of the ferrous sulfate reaction, in which the energy absorbed by the solution was measurd with an extrapolation ionization chamber for which the Bragg-Gray principle was valid. It was apparent, in the case of electrons, that discrepancies in the published values of W, the energy required to produce one ion pair, for various gases, introduced an uncertainty into all energy measurements performed with ionization chambers. It was also apparent that this technique could be used for accurate determinations of W for any gas, provided an accurate G value could be obtained by an independent measurement. Two such measurements are available at the present time: 15.45 ions/100 ev by cathode-ray bombardment techniques[2] and 15.8 ions/100 ev by calorimetry.[3] Perhaps the most significant advantage of this technique is that one may obtain W values using fast electrons without the use of an extremely large chamber, and neither a knowledge of the electron energy spectrum nor the absolute electron disintegration rate is required.

EXPERIMENTAL EQUIPMENT

Measurements were made with x-rays from a $\frac{1}{4}$-in. thick gold target in the Brookhaven Chemistry Department electron Van de Graaff generator operated at 2 Mv. It was assumed that the average x-ray energy was of the order of 1 Mev.[4] A copper absorption curve showed no detectable low-energy components (<100 kev), and therefore photoelectric processes could be ignored.

The parallel plate ionization chamber, based upon a design of G. Failla, is shown in Fig. 1. The plates were made of 1-cm thick polystyrene; their interior surfaces were coated with a thin layer of aquadag. A groove, approximately 0.004 cm wide, 0.005 cm deep, and 2.54 cm in diameter, was scribed on the rear plate to provide the collecting electrode and guard ring. The cable connectors were type BNC Teflon insulated, and were mounted so that all air spaces, seen by the collecting electrode, were eliminated. Since the observed ionization current/unit volume in a parallel plate chamber must be extrapolated to zero volume, the chamber spacing could be changed by rotating the rear plate. The ionization currents were measured across a $1.022\times10^7\pm0.5$ percent ohm calibrated resistor[5] with a calibrated vibrating reed electrometer.[6] At all spacings the chamber was operated with a fixed potential gradient which was sufficient to insure saturation.

The chamber spacings at which measurements were taken were determined by a measurement of the chamber capacitance. It was not possible to use an ac bridge capacitance measurement method because of the losses in the aquadag surfaces, and therefore a dc method employing a vibrating reed electrometer as a null detector was used. The vibrating reed air coupling capacitor was calibrated against a guard-ringed capacitor which had been calibrated against a standard air capacitor.[7] The ionization chamber capacity was then obtained in terms of the air coupling capacitor. The resistance between the guard ring and collector was sufficiently high so that drift was negligible. Figure 2 is a plot of $1/C$ as a function of the number of turns of the rear plate from an arbitrary starting point.

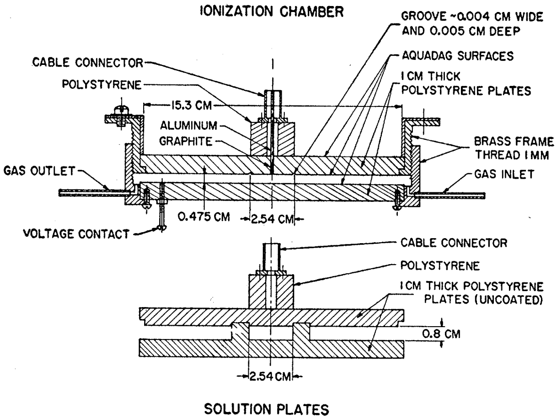

FIG. 1. Drawing of the ionization chamber and the solution plates.

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[1] Weiss, Bernstein, and Kuper, J. Chem. Phys. **22**, 1593 (1954).

[2] R. H. Schuler and A. O. Allen (to be published).

[3] Lazo, Dewhurst, and Burton, J. Chem. Phys. **22**, 1370 (1954).

[4] Miller, Motz, and Cialella, Phys. Rev. **96**, 1344 (1954).

[5] F. M. Glass and R. K. Abele, Rev. Sci. Instr. **21**, 493 (1950). The bridge was calibrated against a standard 10^7 ohm resistor calibrated at the National Bureau of Standards.

[6] Vibrating Reed Electrometer, Model 30, Applied Physics Corporation, Pasadena, California.

[7] Precision Condenser, 722D, General Radio Company, Cambridge, Massachusetts.

For the solution measurements, the chamber plates were replaced with another set of plates (Fig. 1) arranged to provide a cell 2.54 cm in diameter and 0.8 cm high, surrounded with 1 cm thick polystyrene walls. With this arrangement it is possible to reproduce the position of the solution cell and ionization chamber sensitive volume accurately; also the scattered radiation pattern arising from the brass holder and the general environment would be identical for both ionization chamber and solution measurements. The chemical solutions were made using reagent grade ferrous ammonium sulfate, reagent grade sodium chloride, cp sulfuric acid, and distilled water. In all cases the solutions were $10^{-3}M$ ferrous ion, $10^{-3}M$ chloride ion, and $0.8N$ sulfuric acid. Analyses of the solutions were made with a Beckman quartz photoelectric spectrophotometer at a wavelength of 305 mμ, using 2174 for the molar extinction coefficient of ferric ion at 24°C.

The chamber was suspended 34 cm from the gold target for both solution and ionization chamber measurements by three thin steel cables. The chamber position was accurately reproduced each time it was removed by using a positioning device which was attached to the front of the Van de Graaff generator. The various gases were flowed through the chamber at an approximately constant rate; a 10-min flushing period at higher rates was allowed before measurements were begun. Cp tank gases were used, and no special precautions with respect to purity were taken.

Since the x-ray output of the accelerator is dependent upon the operating current and voltage, both of which may fluctuate, the experimental measurements were performed in the following manner. For the ionization current measurements, which were instantaneous measurements, the voltage was maintained constant and the ionization current was recorded as a function of target current. In the case of the solution measurements, it was thought advisable to use a current integrator to record the total radiation received by the solution rather than to try to maintain a constant current. Since the solution irradiation was of the order of 1000 seconds, it was necessary to maintain the voltage constant manually.

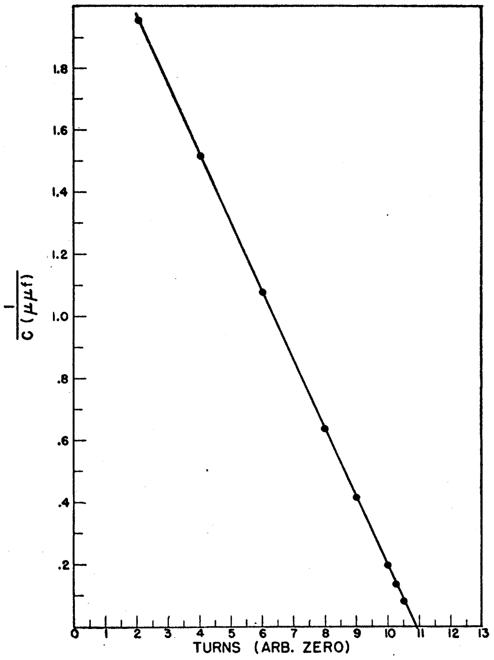

FIG. 2. Plot of reciprocal of the capacitance of the ionization chamber *versus* turns from an arbitrary starting position.

RESULTS

The ionization currents were determined using air, nitrogen, oxygen, carbon dioxide, methane, ethylene, and argon as the chamber fillings. These currents were derived from a least-squares fit to the ionization current-target current curves; in all cases, including the determination of the extrapolation correction, the ionization current corresponding to a target current of 100 μa was used. The ionization currents (normalized to STP and including the extrapolation correction) obtained for the different gases with a chamber volume of 3.39±0.01 cm³ are listed in column 2, Table I. Figure 3 shows the extrapolation curves obtained with air and argon fillings; curves were not obtained for the other gases since their Z was not significantly different from that of air. At the small spacings, measurements were taken with both plus and minus collecting voltage

TABLE I. Summary of experimental data and results.

Gas	Ionization current[a] (10^{-9} amp)	$(NZ)\times10^{20}$[a]	$I(V)$	$K_{\text{gas}}^{\text{poly}}$	$K_{\text{air}}^{\text{gas}}$	W(ev)	$\frac{W_{\text{gas}}}{W_{\text{air}}}$	Mean $W(\text{ev})_{\text{Jesse}}$	$\left(\frac{W_{\text{gas}}}{W_{\text{air}}}\right)_{\text{Failla}}$
Air	3.76±0.07	3.89	83.2[b]	1.040	1.00	33.9±0.8	1.00	34.1	1.00
N_2	3.57±0.04	3.77	80.5[b]	1.036	1.005	24.8±0.5	1.026	34.7	1.034
O_2	4.51±0.05	4.31	92.0[b]	1.053	0.988	30.9±0.5	0.912	30.9	0.914
CO_2	5.92±0.05	5.95	87.4[c]	1.047	0.994	32.6±0.4	0.966	32.9	0.968
A	5.77±0.04	4.85	195.0[d]	1.167	0.891	25.5±0.3	0.751	26.4	···
CH_4	3.61±0.04	2.69	40.5[c]	0.952	1.093	26.8±0.4	0.788	27.3	0.820
C_2H_4	5.75±0.06	4.33	51.4[c]	0.980	1.062	26.3±0.4	0.773	26.3	0.778

[a] Normalized to STP.
[b] Calculated from $I=11.5Z$.
[c] E. Segrè, *Experimental Nuclear Physics* (John Wiley and Sons, Inc., New York, 1953), p. 203.
[d] W. Siri, *Isotopic Tracers and Nuclear Radiation* (McGraw-Hill Book Company, Inc., New York, 1949), p. 79.

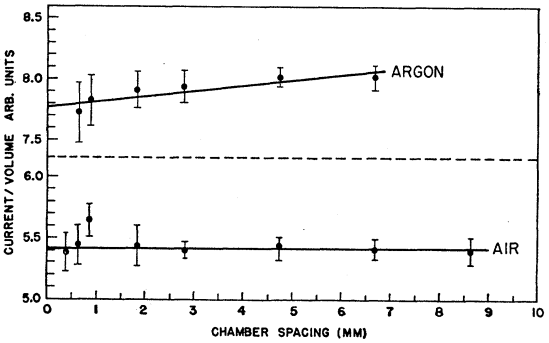

FIG. 3. Extrapolation curves for air and argon fillings.

polarities, and the average current was used to eliminate the contribution of the primary electrons.

It has been shown[1] that the absolute values of W can be calculated from the following equation:

$$W=E\bigg/\left(J\times\frac{(NZ)_{\text{soln}}}{(NZ)_{\text{gas}}}K_{\text{gas}}^{\text{poly}}\right),$$

and that the ratio, $W_{\text{gas}}/W_{\text{air}}$, is given by the following equation:

$$\frac{W_{\text{gas}}}{W_{\text{air}}}=\frac{J_{\text{air}}}{J_{\text{gas}}}\frac{(NZ)_{\text{gas}}}{(NZ)_{\text{air}}}K_{\text{air}}^{\text{gas}},$$

where E = energy absorbed/cc/sec by the solution, J = corrected number of ion pairs/cc/sec, STP, (NZ) = number of electrons/cc, STP, $K_{\text{gas}}^{\text{poly}}$ = stopping power per electron$_{\text{poly}}$/stopping power per electron$_{\text{gas}}$, and $K_{\text{air}}^{\text{gas}}$ = stopping power per electron$_{\text{gas}}$/stopping power per electron$_{\text{air}}$.

The values of $(NZ)_{\text{gas}}$, $K_{\text{gas}}^{\text{poly}}$, and $K_{\text{air}}^{\text{gas}}$ are tabulated in columns 3, 5, and 6, Table I; the number of electrons per cc of solution was 3.42×10^{23} at STP. The quantities, $K_{\text{gas}}^{\text{poly}}$ and $K_{\text{air}}^{\text{gas}}$, were derived from Bethe's equation[8] for the energy loss of electrons. This equation is valid provided the electron energy is greater than the binding energy of the electrons of the gas or wall, and is below 1 Mev so that polarization effect corrections may be ignored. $K_{\text{air}}^{\text{gas}}$ and $K_{\text{gas}}^{\text{poly}}$ were calculated for an electron energy of 128 kev, corresponding to $v/c=0.6$. These quantities vary by less than 2 percent over the energy range, 10 kev–700 kev. In these calculations it was necessary to use values for the average excitation potential; these are listed in column 4, Table I. In the case of compounds, the average excitation potential was calculated from those of the constituent atoms by the Bragg rule; 61 volts were used for the average excitation potential of polystyrene.

The energy absorbed in ev per cc per sec by the solution is given by the following equation:

$$E=\frac{100Y}{G}=OD\frac{N\times100}{\text{time}\times G\times\epsilon}=\text{ev/cc sec},$$

where Y = ferric ion yield (ions/cc sec), G = ferric ions/100 ev, OD = optical density/cm, N = Avogadro's number, and ϵ = extinction coefficient, 2.174×10^6 μmoles^{-1} cc^{-1} cm^{-1}.

In order to correct for the change in solid angle and the absorption of x-rays because of the depth of the solution cell, the solution was extrapolated to zero volume as shown in Fig. 4. Since the energy calibration of the accelerator had changed at the time the solution extrapolation measurements were made, the data shown in Fig. 4 were used only to obtain the magnitude of the correction. The result of 8 determinations was a ferric ion yield of $(3.32\pm0.015)\times10^{13}$ ions/cc sec including the extrapolation correction. It should be pointed out that the 8 determinations included two in which the solution used was the same as that used in the cathode-ray bombardment determination by Schuler and Allen,[2] and in all cases their spectrophotometer and extinction coefficient were used.

The absolute values of W, calculated using the cathode-ray G value of 15.45 ± 0.15 are tabulated in column 7, Table I; the errors listed for W, which include the error in G, are standard deviations. If the calorimetric value of 15.8 ± 0.3 is used, the W values are decreased by the factor 0.975. The ratios $W_{\text{gas}}/W_{\text{air}}$ are tabulated in column 8, Table I. For comparison with other investigations, the W values for the gases based on 26.4 ev for argon as determined by Jesse and Sadauskis,[9] and the W's relative to air determined by Failla[10] are listed in columns 9 and 10, Table I.

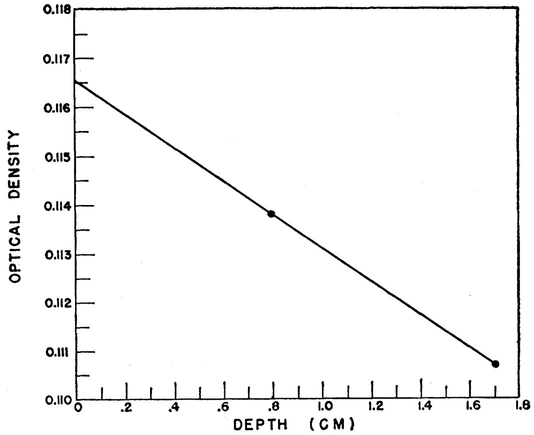

FIG. 4. Extrapolation curve for solution cell.

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[8] E. Segrè, *Experimental Nuclear Physics* (John Wiley and Sons, Inc., New York, 1953), p. 254.

[9] W. P. Jesse and J. Sadauskis, Phys. Rev. **97**, 1668 (1955). We are indebted to W. P. Jesse for informing us of their results before publication.

[10] G. Failla and H. H. Rossi, U. S. Atomic Energy Commission Report, NYO 4582 (unpublished).

The ratios $W_{\text{gas}}/W_{\text{air}}$ are in excellent agreement with the ratios determined by Jesse and by Failla; in both their determinations the stopping power ratio did not enter into the calculations since the total electron energy was absorbed in the gas. In our determination, however, it was necessary to use the stopping power ratios since only a fraction of the electron energy was expended in the gas. The excellent agreement between the two methods indicates that the error in the calculation of the stopping power ratio is small. The absolute values of W for the different gases are also in excellent agreement with Jesse's results; the value of 25.5±0.3 ev obtained for argon is probably low because of the extreme sensitivity of argon to impurities. It should be pointed out that both Jesse and Failla used low-energy electrons in their investigations; these results include considerably higher electron energies. The accuracy of the absolute values of W is, of course, dependent upon the accuracy of the value of G and the calculated stopping power ratios which are used, and also upon the purity of the gases. Further experiments are planned in which the stopping power ratios will be experimentally determined and the purity of the gases will be carefully controlled.

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Measurement of Absorption Coefficients for Photoionizing Radiations in Low-Pressure Gases with a Space Charge Detector*

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A Kingdon cage space-charge detector has been used to measure the production of positive ions in a low-pressure gas due to absorption of photons produced by electron impact excitation in another region of the same gas. Absorption coefficients were measured by changing the source to detector separation. High-purity vacuum techniques were used to avoid contamination of the gas. No ionization was found in hydrogen. For nitrogen the molecular cross section was 4.1×10^{-16} cm^2 and for argon the atomic cross section was 3.1×10^{-16} cm^2. Tentative suggestions are made as to the processes responsible for these total absorption cross sections being much larger than the photoionization cross sections for monochromatic radiations in the ionization continuum region.

THE role of photoionization as an important secondary mechanism in gas discharges, particularly near the anode in asymmetric fields as in the burst pulses and streamers of positive point corona has been extensively discussed by Loeb.[1] A large number of measurements have been made of the absorption coefficients for the radiations producing such photoionization under discharge conditions.[2] Such measurements when carried out at high pressures do not allow accurate evaluation of the very high absorption cross sections required to explain the small distance scale of the burst pulses and streamers. In making measurements at lower pressures it is important to see that any currents measured are due to photoionization arising in the gas and not from photoelectrons emitted from electrodes or walls. The space-charge detector of Kingdon[3] and Hertz[4] seemed ideally suited for this purpose. This operates on the principle that introduction of a few positive ions into the electron space charge of a space charge limited diode gives a large increase in the electron current. The amplification so obtained makes it possible to detect positive ions in the presence of slow electrons.

The Kingdon cage was first applied to the detection of photoionization in gases and vapors by Mohler.[5] It was adapted for measuring relative cross sections for photoionization in alkali vapors by Lawrence and Edlefsen[6] who used two diodes with a balanced technique to eliminate fluctuations due to variations in

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* This work was supported by the Office of Naval Research.

† Currently at the Pacific Naval Laboratory, Esquimault, British Columbia.

[1] L. B. Loeb, *Fundamental Processes of Electrical Discharge in Gases* (John Wiley and Sons, Inc., New York, 1939), Chap. X, Sec. 8, pp. 520 ff.; L. B. Loeb, Phys. Rev. **73**, 798 (1948); **94**, 224 (1954).

[2] E. Greiner, Z. Physik **81**, 543 (1933); A. M. Cravath, Phys. Rev. **47**, 254 (1935); G. Dechene, J. phys. radium **7**, 533 (1936); H. Raether, Z. Physik **110**, 611 (1938); W. Schwiecker, Naturwiss. **28**, 380 (1940); Z. Physik **116**, 562 (1940); S. H. Liebson, Phys. Rev. **74**, 694 (1948); Jaffe, Craggs, and Balakrishnan, Proc. Phys. Soc. (London) **B62**, 39 (1949).

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[5] F. L. Mohler, Phys. Rev. **28**, 46 (1926); Proc. Natl. Acad. Sci. U. S. **12**, 494 (1926).

[6] E. O. Lawrence and N. E. Edlefsen, Phys. Rev. **34**, 233 (1929).