PHYSICAL REVIEW VOLUME 93, NUMBER 6 MARCH 15, 1954

Ionization of Pure Gases and Mixtures of Gases by 5-Mev Alpha Particles

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(Received November 13, 1953)

In this experiment the charge produced in a large ionization chamber, by the complete stopping of Pu^{239} alpha particles, was measured using an accurately calibrated capacitor in series with a potentiometer. An electrometer connected across both the capacitor and potentiometer was used as a null indicator. From the charge produced the number of ion pairs n was deduced and W, defined by the equation $W=E/n$ where E is the energy used in forming the n ion pairs, was computed.

For pure gases, we found the following values of W (in ev per ion pair): A, 26.4 ± 0.3; BF_3, 36.0 ± 0.4; C_4H_{10}, 26.4 ± 0.3; CO_2, 34.3 ± 0.3; C_2H_4, 28.0 ± 0.3; He, 46.0 ± 0.5; H_2, 37.0 ± 0.4; CH_4, 29.4 ± 0.3; N_2, 36.3 ± 0.4; O_2, 32.2 ± 0.3; SF_6, 35.7 ± 0.4; air, 35.0 ± 0.3; freon 12, 29.5 ± 0.3.

Our results for W for a mixture of gases are described by the formula

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

where $z=P_1/(P_1+aP_2)$, and W_m is the W for the gas mixture having two components of pressure P_1 and P_2 with W values for the pure gases equal to W_1, and W_2, respectively. For the following mixture a has the values shown: N_2-H_2, 0.28; N_2-A, 0.53; N_2-O_2, 1.06; He$-$A, 0.75; $He-H_2$, 3.55; $He-N_2$, 8.47; $He-CH_4$, 0.68; $A-H_2$, 0.56; H_2-CH_4, 4.03.

In the case of He the W of 46.0 is not used in the above equation, since small traces of impurities reduce W(He) to 30.0 electron volts, and this latter value is appropriate for using in the formula for gas mixtures.

INTRODUCTION

SOME of the practical radiation dosimetry units are defined in terms of the energy delivered by the radiation to a gram of soft tissue. Methods of measuring dose, on the other hand, involve the use of Bragg-Gray cavities filled with various gases in which ionization is collected. Thus, to have a consistent system of definitions and measurements, the value of W (electron volts required to produce an ion pair) must be known. It is known that the value of W depends, in general, on the mass and energy of the ionizing particle, and the gas used. It is the purpose of this work to study a large number of gases and gas mixtures, using a fixed particle and energy; namely, Pu^{239} alpha particles. Many of these gases have been studied previously, but unfortunately some of the work has been hampered by impure gases and other difficulties.

APPARATUS AND METHOD

The method used for measuring the ionization produced by alpha particles is shown in Fig. 1. The parallel plate ionization chamber is enclosed in a steel case which may be held at positive pressures so that the range of alpha particles will be entirely inside the collecting volume even for gases such as hydrogen or helium. The rate of ionization in the chamber is measured by the voltage change on an accurately calibrated capacitor. The voltage change is determined

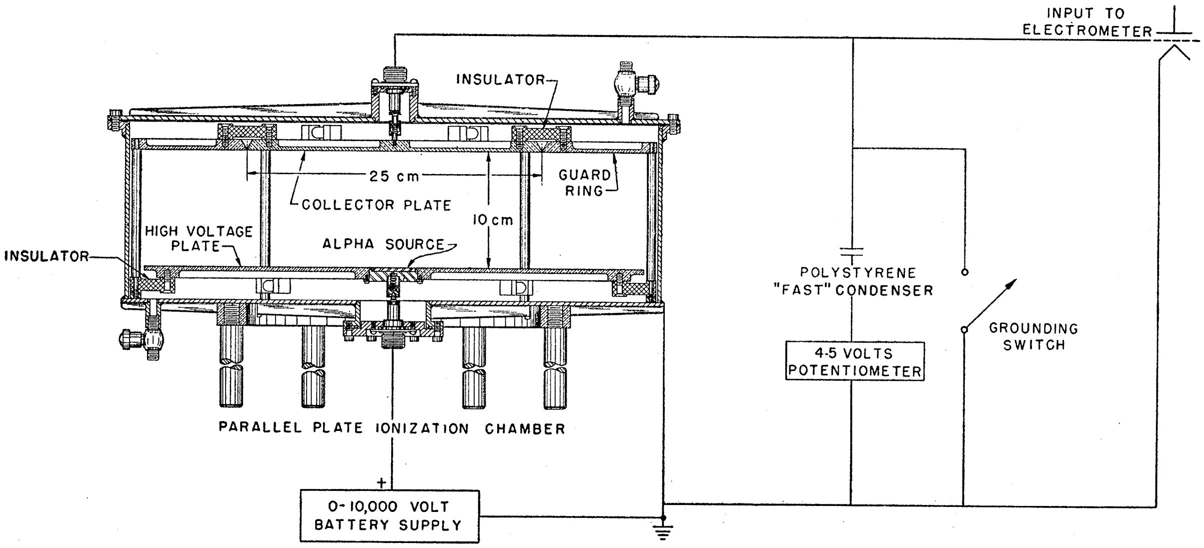

FIG. 1. Block diagram of the apparatus for measuring W for alpha particles.

with a potentiometer, using an ac-operated electrometer[1] as a null indicator. The capacitor is of such size that the readings are several hundred millivolts per minute, a rate of drift which is much greater than that due to the inherent variations in the electrometer. For this system, the formula appropriate for computing W is:

$$W = N \times E \times 1.59 \times 10^{-19} / CV, \qquad (1)$$

where N = counts per minute of alpha source with 2π geometry, E = energy of alpha particles in electron volts, C = capacitance of the condenser in farads, V = rate of drift of the condenser (volts/minute), and 1.59×10^{-19} = charge of the electron in coulombs. An alpha source of Pu^{239} is electroplated on platinum and calibrated by counting with a methane flow proportional counter connected to a linear amplifier and discriminator circuit. The source plate is used without a collimator since with a collimator some ionization is formed in the sensitive volume by alpha particles which terminate in the collimator wall without losing all their energy in the gas. These pulses would not be detected with the proportional counter but do contribute to the ionization.

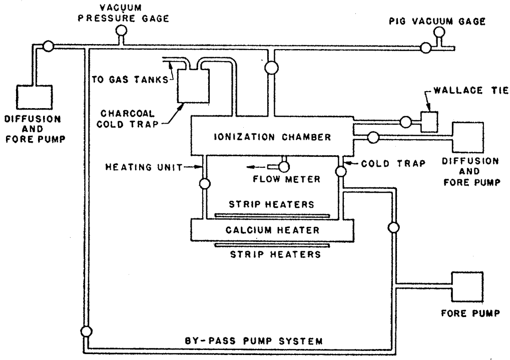

FIG. 2. Block diagram of gas filling and purification system. All circles, unless otherwise designated, are cut-off valves.

An extremely stable high-voltage supply is required and for this reason a series of 300-volt batteries, connected by resistors for safety, is mounted in a polystyrene box. This system gives results that are reproducible to within 0.1 percent.

Purification of the different gases is accomplished by means of the apparatus in Fig. 2. Gases which condense in a trap of liquid nitrogen are redistilled, while others are run through activated charcoal at liquid nitrogen temperature. Figure 2 also shows a calcium trap attached by one-inch stainless steel tubes to the ion chamber. Convection of the gas through the calcium trap and the chamber was increased by placing a heating coil on one of the chamber outlets, which was kept at 300°C and by a liquid nitrogen trap on the other chamber port. If the gas itself does not unite with hot calcium, this method of purification is often used to remove certain impurities. In the case of helium, the calcium is kept at a temperature of 400°C and proved to be very effective in removing oxygen. Argon contamination is removed by flowing through a trap of charcoal at liquid nitrogen temperature.

TABLE I. W values (electron volts per ion pair) for nonelectronegative gases.

Gas	Our result	Reference result
Argon	26.4±0.3	26.4[a]
Boron trifluoride	36.0±0.4	
Butane	26.4±0.3	
Carbon dioxide	34.3±0.3	34.5[a]
Ethylene	28.0±0.3	28.0[a]
Helium	46.0±0.5	42.7[a]
Hydrogen	37.0±0.4	37.0[b]
Methane	29.4±0.3	29.0[b]
Nitrogen	36.3±0.4	36.3[c]

[a] See reference 3.
[b] See reference 4.
[c] See reference 2.

RESULTS WITH PURE NONELECTRONEGATIVE GASES

Nonelectronegative gases are defined as those in which the probability of electron attachment to form a heavy negative ion is small. Thus, the chances of columnar recombination are small at moderate electric fields, and the ionization current *versus* voltage curve quickly saturates. Table I shows the W values obtained for pure gases.[2–4]

Helium requires very careful purification; with no purification grade A helium[5] taken from different tanks gave a spread of W values from 31 to 43 electron volts. Two different methods of purification gave W for helium equal to 46.0±0.4 electron volts. One method consisted of flowing helium over cocoanut charcoal at

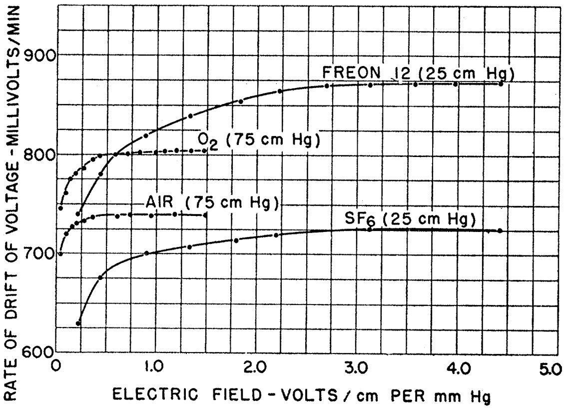

FIG. 3. Saturation curves for SF_6, air, O_2, and freon 12.

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[1] F. M. Glass, Nucleonics 10, No. 2, 36 (1952).

[2] Alder, Huber, and Metzger, Helv. Phys. Acta 20, 234 (1947).

[3] W. P. Jesse, and J. Sadauskis, Phys. Rev. 90, 1120 (1953).

[4] J. M. Valentine and S. C. Curran, Phil Mag. 43, 964 (1952).

[5] According to information supplied by Dr. M. M. Deaton, Chief, Research Branch, Helium Division, Region IV, Bureau of Mines, grade A helium has a purity of 99.9+ percent when bottled.

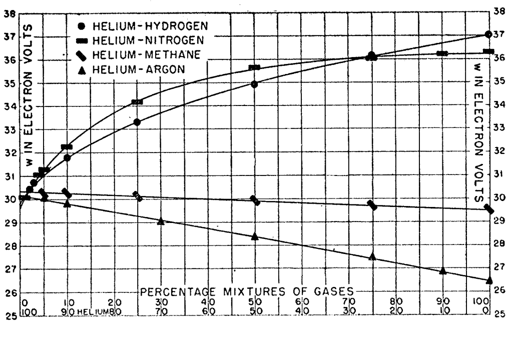

FIG. 4. W for mixtures of He with H_2, N_2, CH_4, and A.

liquid nitrogen temperature; the ionization being measured during flow. Stopping the flow results in a rapid decrease in W (increase in ionization) after a few minutes. This was probably due to outgassing of the chamber even though no gas other than helium had been in the chamber for over 90 days. The second method of purification consisted of a continuous convection of the helium over metallic calcium held at 400°C.

TABLE II. W values for electronegative gases.

Gas	W in ev
O_2	32.2±0.3
SF_6	35.7±0.4
Air	35.0±0.3
Freon 12	29.5±0.3

RESULTS WITH ELECTRONEGATIVE GASES

For electronegative gases columnar recombination is quite appreciable even with high electric fields in the ionization chamber. Results of ionization current *versus* electric field (in volts per cm per mm Hg) are shown in Fig. 3 for SF_6, O_2, freon 12, and air. The curve shown for air was the same for dry air (made by mixing N_2 and O_2) and air taken from the atmosphere at 53 percent relative humidity. An extrapolation of the saturation curves by means of the Jaffe theory[6] resulted in only a very minor increase in current above its value at the highest fields; thus the chamber was known to be very near saturation. Values for W can be computed using the upper value for the current, and these values for electronegative gases are given in Table II.

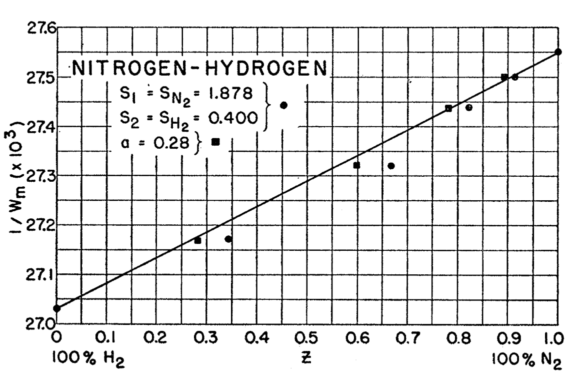

FIG. 5. $1/W_m$ as function of z for N_2-H_2 mixture.

RESULTS WITH GAS MIXTURES

Since the W for He depends so critically on the amount of gas impurity it is of interest to obtain W curves as a function of gas mixture for He with several other gases. In Fig. 4 these values are shown for H_2, N_2, CH_4, and A, in helium. In each case the W is reduced from 46.0 ev for pure He to approximately 30 ev by the addition of small traces (less than one percent) of the contaminating gas. This behavior is consistent with the suggestion by Jesse and Sadauskis[7] that the low reported values for W of He are due to the fact that the energy in the well-known metastable state in He (19.7 volts) can be transferred to a contaminating gas and produce extra ionization in gases where the ionization potential is less than the metastable potential.

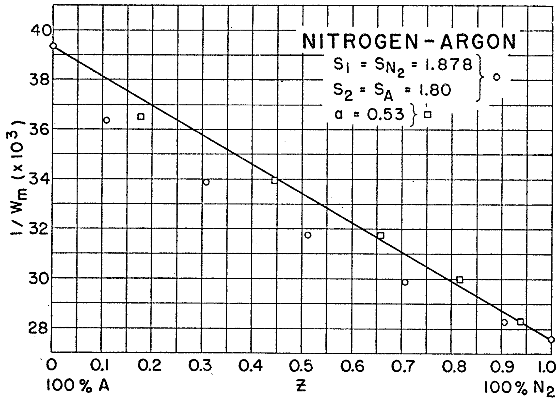

FIG. 6. $1/W_m$ as function of z for N_2-A mixture.

If it is assumed that the presence of a second gas does not contribute ionization to the first, then a formula may be written for the W of a gas mixture. Such a formula,[8] based on the energy lost to the two gases according to the partial pressures P_1 and P_2, and the molecular stopping powers S_1 and S_2, may be written as:

$$\frac{1}{W}=\left(\frac{1}{W_1}-\frac{1}{W_2}\right)z+\frac{1}{W_2}, \tag{2}$$

where

$$z=S_1P_1/(S_1P_1+S_2P_2).$$

Plotting the measured values of $1/W$ as a function of z should give a straight line according to Eq. (2). Our results for several gas mixtures are shown in Figs.

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[6] G. Jaffe, Ann. Physik 42, 303 (1913). A convenient application was made by H. Zanstra, Physica 2, 817 (1935).

[7] W. P. Jesse and J. Sadauskis Phys. Rev. 88, 417 (1952).

[8] Huber, Baldinger, and Haeberli, Helv. Phys. Acta, 23, Suppl. III (1949).

5-13, where it is seen that using reported[9] values for (RaC alpha) molecular stopping powers gives large deviations (small circle in figures) for almost all cases except for N_2-O_2 and H_2-CH_4 mixtures. In a subsequent article, Haeberli, Huber, and Baldinger[10] noticed small deviations from Eq. (2) for mixtures N_2-He and He—A. Our difference for the He—A mixture is much larger and is not due entirely to the fact that we use $S_{He}=0.308$ while they use a relative value of 0.430.

In order to account for the small differences in theory and experiment, Haeberli *et al.*, assumed that a certain portion E_s of the alpha-particle energy is used in forming delta rays, and that the delta-ray energy is divided between the two gas components in proportion to the stopping powers of the two gases for delta rays (σ_1,σ_2). The amount of ionization produced by the secondary electrons (delta rays) is proportional to E_s and inversely proportional to the W values for delta rays (W_{s1},W_{s2}). These assumptions lead to a modified formula for the W of a gas mixture:

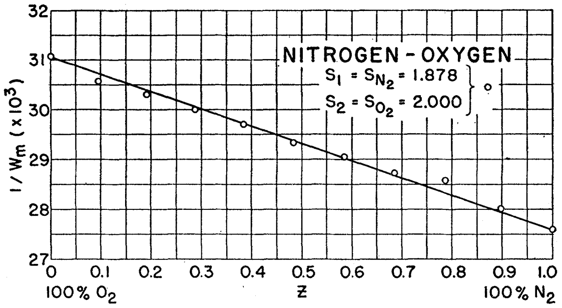

FIG. 7. $1/W_m$ as function of z for N_2-O_2 mixture.

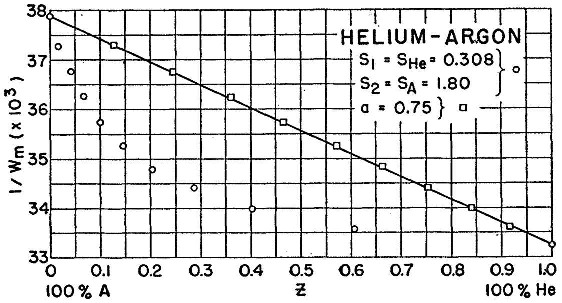

FIG. 8. $1/W_m$ as function of z for He—A mixture.

$$\frac{1}{W_m}=\left(\frac{1}{W_1}-\frac{1}{W_2}\right)z+\frac{1}{W_2}+\Delta, \tag{3}$$

where

$$\Delta=\left(\frac{1}{W_{s1}}-\frac{1}{W_{s2}}\right)(k_2-k_1\gamma_{12})\frac{z(1-z)}{\gamma_{12}+z(1-\gamma_{12})},$$

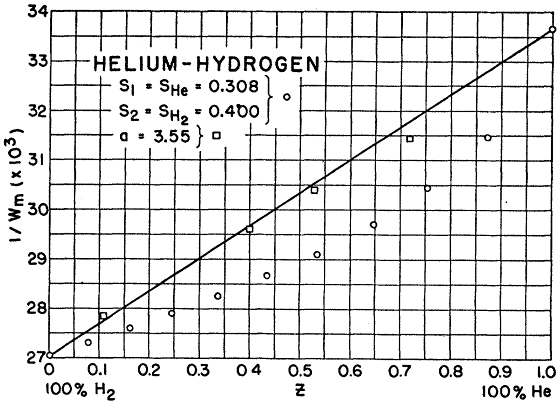

FIG. 9. $1/W_m$ as function of z for $He-H_2$ mixture.

with $\gamma_{12}=s_1\sigma_2/s_2\sigma_1$; k_2 and k_1 are defined by $E_s=k_1E_1+k_2z_2$, where $E_1=zE_0$, $E_2=(1-z)E_0$, and E_0 is the initial energy of the alpha particle. For a given gas mixture, the Δ term should depend on pressure (or z) as

$$\Delta=A\frac{z(1-z)}{\gamma+z(1-\gamma)}, \tag{4}$$

where A is a constant for a given mixture. Thus, the difference in theory and experiment is accounted for by using the appropriate values for γ and A.

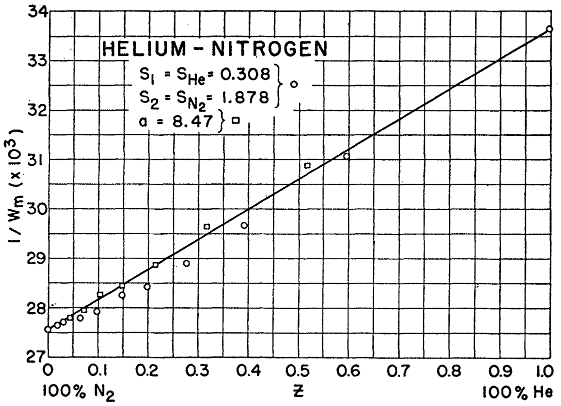

FIG. 10. $1/W_m$ as function of z for $He-N_2$ mixture.

If it were assumed that the "effective" stopping power for insertion in z in Eq. (2) is not the actual

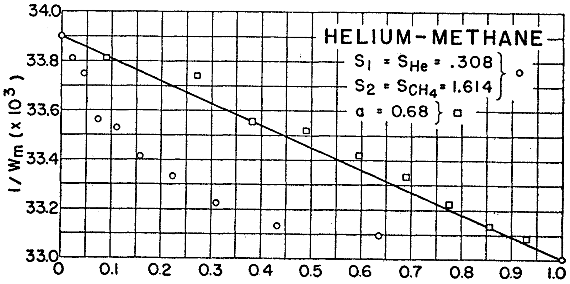

FIG. 11. $1/W_m$ as function of z for $He-CH_4$ mixture.

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[9] H. R. von Taubenberg, Z. Physik 2, 268 (1920).

[10] Haeberli, Huber, and Baldinger, Helv. Phys. Acta, **26**, 145 (1953).

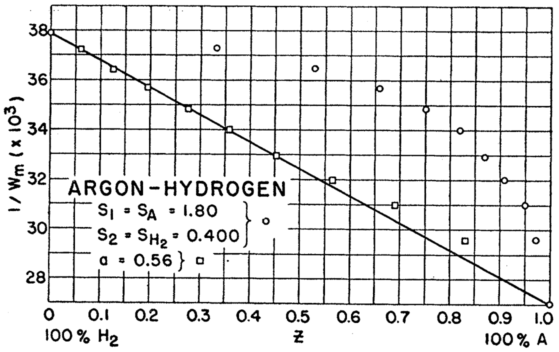

FIG. 12. $1/W_m$ as function of z for $A-H_2$ mixture.

stopping power reported in the literature, but differs from S_1 by an amount ΔS, then we would write

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

$$=\left(\frac{1}{W_1}-\frac{1}{W_2}\right)\Delta z, \quad (5)$$

where

$$\Delta z=\frac{(S_1+\Delta S_1)P_1}{(S_1+\Delta S_1)P_1+S_2P_2}-\frac{S_1P_1}{S_1P_1+S_2P_2},$$

if it is assumed that S_1 is changing while S_2 is fixed.

Now we may write for Δz,

$$\Delta z=\frac{\Delta S_1P_1}{S_1P_1+S_2P_2}-\frac{S_1P_1}{S_1P_1+S_2P_2}\cdot\frac{\Delta S_1P_1}{S_1P_1+S_2P_2+\Delta S_1P_1}$$

$$-\frac{(\Delta S_1P_1)^2}{(S_1P_1+S_2P_2)(S_1P_1+S_2P_2+\Delta S_1P_1)}, \quad (6)$$

and if the term in $(\Delta S_1)^2$ is neglected,

$$\Delta z=\frac{\Delta S_1}{S_1}\times\frac{z(1-z)}{1+(\Delta S_1/S_1)z}, \quad (7)$$

and

$$\Delta\left(\frac{1}{W_m}\right)=\left(\frac{1}{W_1}-\frac{1}{W_2}\right)\times\frac{\Delta S_1}{S_1}\times\frac{z(1-z)}{1+(\Delta S_1/S_1)z}$$

$$=\frac{Bz(1-z)}{1+bz}, \quad (8)$$

where

$$B=\left(\frac{1}{W_1}-\frac{1}{W_2}\right)\frac{\Delta S_1}{S_1} \quad \text{and} \quad b=\frac{\Delta S_1}{S_1}.$$

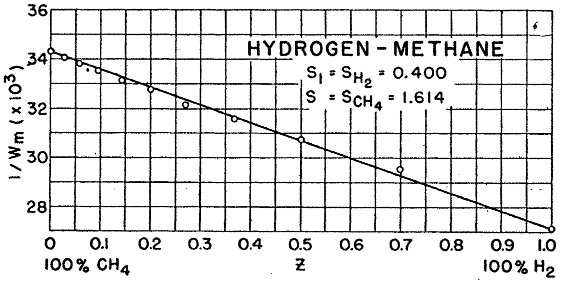

FIG. 13. $1/W_m$ as function of z for H_2-CH_4 mixture.

The form of Eq. (8) is precisely the same as Eq. (4) with $B=A/\gamma$ and $b=[(1-\gamma)/\gamma]$. The facts that the form of Eqs. (8) and (4) are identical and that Eq. (4) was used to account for differences in W values due to delta rays while Eq. (8) was used to account for differences in the effective stopping powers (due either to fact that the arithmetic average values for a given initial energy in a particular gas is not correct for insertion into Eq. (2) for gas mixtures, or that errors exist in reported values) suggests that a general formula (which will include both of the above effects) can be written for the W of a gas mixture as follows:

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

where

$$z=P_1/(P_1+aP_2). \quad (9)$$

TABLE III. Values of a compared to S_2/S_1.

Mixture	Figure	S_2/S_1	a
N_2-H_2	5	0.21	0.28
N_2-A	6	0.95	0.53
N_2-O	7	1.06	1.06
$He-A$	8	5.85	0.75
$He-H_2$	9	1.30	3.55
$He-N_2$	10	6.10	8.47
$He-CH_4$	11	5.24	0.68
$A-H_2$	12	0.22	0.56
H_2-CH_4	13	4.03	4.03

The constant a is determined empirically for every mixture and is equal to S_2/S_1 in cases where Eq. (2) holds.

As seen from the curves in Figs. 5–13, the agreement between measurements and Eq. (9) is good when the correct value of a is used. Comparisons of a with S_2/S_1 are made in Table III. It should be noted that for He the W for "contaminated He" was used as 30.0 ev.

Strictly speaking, the approximation made in deducing Eq. (7) is not justified in view of some of the values of a in Table III. In any case, the argument presented is not intended to be a proof that the empirical Eq. (9) holds for every mixture. However, the identical form of Eqs. (4) and (8) implies that not all the deviations found by Haeberli *et al.*, should be attributed to delta-ray formation. Furthermore, Eq. (9) has some value in that it is not only an extremely simple way to represent large amounts of experimental data, but is useful in attempting to separate sudden changes (due, for example, to the discharge of metastable states) in $(1/W)$ as a function of z from the more gradual ones that Eq. (9) is intended to represent.

ACKNOWLEDGMENTS

The authors are grateful for the many helpful suggestions of J. Neufeld and R. H. Ritchie of the Health Physics Division. We wish also to express appreciation to R. E. Zedler of the Instrument Department for his work in designing the ionization chamber, and to P. N. Hensley of the Engineering Department who designed parts of the gas purification system.

PHYSICAL REVIEW VOLUME 93, NUMBER 6 MARCH 15, 1954

Proton Relaxation in Water

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(Received November 2, 1953)

A determination of the thermal relaxation time of protons in pure water gives the value 3.6±0.2 sec, in very good agreement with theory. The O_2 molecule in aqueous solution seems to have a μ_{eff} of 1.2 Bohr magnetons for the relaxation processes.

We have recently performed a series of measurements of the thermal relaxation time of protons in pure water and in water containing oxygen in solution. The methods used are based on measurements of amplitude of the "in phase" nuclear signals caused by the total reversal of the magnetization. Two observations with different sweep frequencies and with resonance field centered with respect to the sweep, or one observation with resonance field not centered (Fig. 1), enable one to determine the relaxation time. This latter method is similar to that used by Conger and Selwood.[1] To obtain good accuracy with the first method, one of the two sweep periods must be several times greater than the relaxation time. We have therefore arranged a device for observation and registration of the nuclear signals with modulation frequencies of the constant field as low as 0.02 cycle/sec.

We find with both methods $T_1 = 3.6 \pm 0.2$ sec for the thermal relaxation time of protons in water completely free of oxygen and $T_1 = 1.4 \pm 0.1$ sec for water saturated with oxygen at a pressure of one atmosphere. The time we find for pure water is considerably different from that found by Purcell *et al.*[2] (2.3 sec), but it is in very good agreement with their theory if one assumes for the rotation of the water molecule a correlation time of 1×10^{-11} sec and for the translational motion of two molecules separated by a distance r a correlation time equal to the time they take to travel over the distance r. Our result seems to justify this assumption.

Our measurements show that the influence of oxygen in solution, which was already noticed in the first observations of Bloch *et al.*,[3] is smaller than one could expect from the magnetic moment of the oxygen molecule which is 2.8 Bohr magnetons. The μ_{eff} of the O_2 in the relaxation processes seems to be 1.2 Bohr magnetons. This could be caused by the formation of molecular complexes (like O_4 molecules with a zero moment), or by the influence of the electronic relaxation on the correlation time. This latter process seems to influence the nuclear relaxation also in other cases.[2,4]

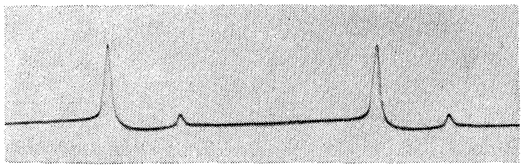

FIG. 1. "In phase" proton signals in pure water due to total reversal of the magnetization. Resonance field not centered with respect to the sweep. Sweep period, 5.7 sec.

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[1] R. L. Conger and P. W. Selwood, J. Chem. Phys. **20**, 383 (1952).

[2] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948); N. Bloembergen, *Nuclear Magnetic Relaxation* (M. Nijhoff, The Hague, 1948).

[3] Bloch, Hansen, and Packard, Phys. Rev. **70**, 474 (1946).

[4] R. L. Conger, J. Chem. Phys. **21**, 937 (1953).