# PRECISE MEASUREMENTS OF W, THE MEAN ENERGY EXPENDED PER ION PAIR FORMED IN ALKANE VAPORS AND IN ARGON

A Dissertation Presented to the Faculty of the Department of Chemistry College of Arts and Sciences University of Houston

> In Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy

> > by Thomas Ash Stoneham December 1970

For the welfare of mankind; to the glory of God.

To the happiness of my darling wife, our lovely children and our wonderfully gracious families.

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#### ABSTRACT

Ionization currents were measured for the complete stopping of Ni-63 beta rays in nitrogen, in argon, in the normal alkanes through heptane and in the branched chain alkanes through hexane. Values of W, the mean energy expended per ion pair formed, were determined from the ratio of ion current in nitrogen to that in the sample, relative to the W for nitrogen, 34.6 eV [G. N. Whyte, Radiation Res. <u>18</u>, 265 (1963)]. W(beta) values for alkanes were measured with a precision of ca. 0.1% and that of argon within 0.2%. No variation of W was experienced as pressures were increased by a factor of two, up to 2700 torr. There is also no temperature dependency in argon, methane, ethane and propane in the 25° to 200° C range.

Energy balance considerations reveal that at least half of the energy absorbed in the complete stopping of electrons in vapors of normal alkanes  $C_1$  to  $C_5$  is expended in ionization, while about one third goes into excitation and the rest remains in subexcitation electrons.

W(beta) correlates well with molecular structure in the normal and branched alkanes. Ionization potentials  $(I_0)$  as well as W's may be predicted empirically by extrapolating values from tables of W,  $I_0$ , and W/I<sub>0</sub>.

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## INTRODUCTION

#### INTRODUCTION

The primary processes in the irradiation of molecular systems may be considered in terms of time elapsed from the instant of impact of the ionizing radiation. Within  $10^{-15}$  seconds, an ion pair may be formed, either singly or multiply ionized, in any of a number of electronically or vibrationally excited states or an excited neutral may be formed initially. Following the time required for at least one vibration (ca.  $10^{-13}$ seconds), other species may be present. An excited ion may dissociate into fragments. An excited neutral may dissociate into neutral fragments or into an ion pair. After sufficient time for at least one collision (ca.  $10^{-10}$  seconds at a pressure of one atmosphere)<sup>1</sup> an ion may be neutralized; an excited neutral may be deactivated.

The distribution of energy into ionic and neutral processes may be expressed as an energy balance

$$T_o = N_i (\overline{E}_i + \overline{E}_{se}) + N_x \overline{E}_x$$

in which an incident particle of energy  $T_0$  imparts a mean amount of energy ( $\overline{E}_i + \overline{E}_{se}$ ) to a number ( $N_i$ ) of ions and subexcitation electrons and a mean amount of energy  $\overline{E}_x$  to a number ( $N_x$ ) of neutral excited species. The quantity  $T_0/N_i = W$ , the mean energy expended in the system per ion pair formed, is a property of the aggregate system of molecules. W is used widely in radiation dosimetry,<sup>2-9</sup> and in the study of energy deposition mechanisms.<sup>10-14</sup>

#### A. Review of the Literature

Extensive studies of W over the past two decades have led to an understanding of experimental factors which influence ionization measurements, such as the effect of source type and source energy and the enhancement of ionization of rare gases by contaminants.<sup>15-22</sup> The list of substances for which W has been measured has been lengthened and different experimental techniques have been developed during the past ten years.<sup>5</sup>,19,**2**3-**3**9 The topic has been reviewed repeatedly<sup>4</sup>,11,14,40-42 and several attempts have been made to account for these measurements on a theoretical basis.<sup>12-14</sup>, 43-45

Recent improvements in the calibration of electronic components and radiation sources have enhanced the precision of ionization current measurements and the accuracy of absolute W measurements.<sup>28,37,46</sup> Subsequently a more detailed view of ionization as a function of particle energy has become possible.<sup>19,20,35</sup> There is an appreciable difference between the energy required for ionization by alpha-particles and by electrons and electromagnetic radiation,<sup>35-37</sup> which has been attributed to a change in the mode of energy loss as the alpha-particle approaches thermalization and is neutralized to form a Helium atom.<sup>14,32</sup> On the other hand, W-values measured for all types of electron sources, W(beta), appear to be independent of source type and source energy.<sup>40,46-48</sup> Energy dependence studies with alpha sources have demonstrated a decrease in W(alpha) with increasing energy of the source<sup>19,20,35</sup> and that W(beta) is the lower limit to possible values of W(alpha). In contrast to the

single degradation spectrum of beta-particles where all energy loss is by electrons, there are separate degradation spectra for alpha particles and their secondary electrons. 11,49 W(beta) is therefore the more fundamental property and has applicability to a variety of sources; our further discussion will be confined to this quantity.

A considerable variety of conditions have been used for the measurement of W(beta) since 1955. Table I includes descriptive information regarding the experimental approach of a number of workers. Chambers ranged in size from the extrapolation chamber of Weiss and Bernstein<sup>50,51</sup> with .475 cm plate spacing, to the large cylinder of Jesse and Sadauskis, which was 20.5 cm in diameter and 21.0 cm long with a 17 cm diameter collecting electrode.<sup>46</sup> Types of ionizing radiations included beta-rays from a number of isotopes, <sup>19,22,23,28,52-56</sup> accelerated electrons, <sup>5,47</sup> gamma-rays, <sup>29,30,38</sup> and X-rays. <sup>25,26,50,51,57</sup> Pressures ranged from 50  $torr^{50}$  to 600  $torr^{54}$  and temperatures from zero degrees centigrade<sup>47</sup> to 150 degrees centigrade.<sup>23</sup> W(beta) values reported for some alkanes, nitrogen and argon are shown in Table II. Average deviations from the mean of reported values are shown in order to demonstrate the discrepancies among the values published. Even recent reports differ by more than 3% although precision of individual measurements is reported to be much better.

B. Statement of the Problem

It is the objective of this work to provide reliable and precise

values of W(beta) for argon and a number of alkanes, beginning with the lighter compounds, and to assess their dependence upon temperature and pressure.

There are two basic techniques for determining W(beta). One method, which may be used with electromagnetic radiation and accelerated electrons, allows incident radiation from an external source to pass completely through the chamber. An electric field is applied sufficient to eliminate homogeneous recombination of opposite charges so that a saturation current may be measured. Relative W-values are obtained from measured ion currents and the ratios of known stopping powers. Even the most recent studies using this method report a precision of only 1% to 2%.<sup>29,30,38</sup> The other method requires the complete stopping of betarays within a chamber. A high gas pressure is used so that the range of the particle is less than the distance between the source and the wall. The latter technique was chosen for this work because of its superior precision.<sup>23,28,46,56</sup>

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### EXPERIMENTAL

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#### EXPERIMENTAL

#### A. Materials

Research Grade Nitrogen (99.9995%) (Matheson Gas Products Co.) and High Purity Dry Nitrogen (99.995%) (Iweco, Inc.) were used without further purification and gave indistinguishable results. All alkanes were Research Grade (99.9%) (Matheson Gas Products and Phillips Petroleum Co.) except 2,2-dimethylbutane and 2,3-dimethylbutane which were Pure Grade (99%) (Phillips Petroleum Co.) and propane which was Chemically Pure Grade (99%) (Matheson Gas Products Co.). Research Grade ethane (Phillips) and Chemically Pure Grade propane (Matheson) were analyzed in our laboratory by gas chromatography and found to contain .1% and .4% impurities, respectively.<sup>58</sup> (The principal impurity in both gases was 2-methylpropane.) Liquid samples were degassed by the pump-freeze-thaw method and the subsequent saturation currents were again indistinguishable from those of untreated samples. A complete list of the samples used and their purities as stated by the suppliers is given in Table III.

#### B. Apparatus

The ionization chamber (Figure 1) was a stainless steel sphere, radius 6.2 cm, (Cary Instruments) with a triaxial ceramic-to-metal feed-thru constructed for us by Ceramaseal Inc. (No. 804 B 5757-1, Rev. C.). A 1 mm thick, 3 mm wide brass ring of 2.5 cm radius was attached to the center lead of the feed-thru via a stainless steel rod. A set of ten parallel .010 inch diameter wires (82% Cu. 18% Ni-Ag alloy) were lashed to the ring at 1/9 inch intervals. The central one-inch square area of the grid was electroplated (Hastings Radiochemical Works) from a solution of  $^{63}$ NiSO<sub>4</sub> (specific activity 11 c/g.) to a total activity of ca. 2.6 millicuries measured as described below. Statistical fluctuation of the beta current between measurements is less than .005%. The grid structure also served as the charge collecting electrode and was shielded by the grounded intermediate conductor of the triaxial feed-thru. The chamber wall was connected to a Fluke Model 415B high voltage supply and insulated from the gas-handling system by a ceramic-to-metal tube seal (Latronics Corporation part number 35.5500).

The gas-handling system (Figure 2) was constructed of 1/2 inch stainless steel tubing with stainless steel bellows valves (Hoke, Inc. and Nupro Co.). A two-inch oil diffusion pump (Consolidated Vacuum Corporation type PMCS-2C) with a chilled water trap, backed by a 5 cfm mechanical pump was used for evacuation. Vacuum was measured by a cold cathode discharge gauge (NRC Equipment Corporation No. 524-1). Above 1 torr a non-bonded strain gauge transducer (Consolidated Electrodynamics Corporation No. 4-316) was used to measure pressures with ± 1 torr accuracy employing the null mode against a 2 meter mercury manometer. Gases were introduced via a short polyethylene line containing a stainless steel needle valve with teflon packing. Liquids were evaporated into the system from a stainless steel cylinder which was attached to the inlet with a Cajon V-C vacuum fitting.

An oven of two-inch Marinite housed the chamber and gas-handling system. Two rod heaters powered by Variac auto-transformers and two coil heaters actuated with bimetallic thermoregulators (Fenwal, Inc. type 17502) were employed to achieve temperature control. Six ironconstantan thermocouples were used to monitor thermal gradients, which did not exceed 5° C when the oven was at 200° C. The actual temperature was read from a mercury thermometer suspended an inch from the chamber. The estimated uncertainty of the chamber temperature is  $\pm 2^{\circ}$  C.

#### C. Method of Measurement

The gas-handling system was pumped overnight before beginning the experiment for each sample. After preliminary measurements on  $N_2$ , the system was again pumped to less than one micron pressure for at least 15 minutes before introducing the sample.

Pressures to be used were predetermined whenever possible, from considerations of range of 66 keV electrons in the samples to be used.<sup>59-61</sup> In cases where this information was not available, minimum pressures were estimated by interpolating electron densities calculated from the van der Waals equation (Appendix A) since the stopping power of electrons in a medium is proportional to its electron density and also inversely proportional to the range. For electrons the Bethe stopping power equation is<sup>7</sup>

 ${}_{m}S = \frac{2\pi e^{4}NZ}{Am_{o}v^{2}} \left[ \ln \frac{m_{o}v^{2}T}{4(1-\beta^{2})I^{2}} + 1 - \beta^{2} + (\frac{T}{W})^{2}(\frac{1}{8} + \ln 2) - \delta \right] \text{ where } v = \beta c \text{ is}$ the velocity of the particle,  $W = T + m_{o}c^{2}$  is the total energy of the electron, I is the mean excitation energy of the atomic or molecular system, e is the charge on the electron, N is the number density of atoms in the medium, Z is the atomic number, A is the atomic weight, and  $\delta$  is a polarization correction. To a good approximation, relative stopping powers are proportional to relative electron densities,  $(N_1Z_1/A_1)/(N_2Z_2/A_2)$ , and according to Bragg's rule<sup>7</sup> the atomic parameters are additive in molecular systems. After determining the minimum pressure required to reduce the beta-rays from  $E_{max}$  to thermal energy in the gas before reaching the chamber wall, a series of pressures was chosen, including the minimum, the maximum obtainable in our system (2700 torr) and others equally spaced. The median pressure was run first, then the highest, lowest, etc., and finally the median again. This sequence was designed to cause any effect attributable to accumulated products or impurities to appear as random error after all values were corrected with respect to the difference between the first and last sample measurements.

Currents were measured using a beam current integrator (Tomlinson Research Instruments Corporation Model 2000) whose maximum input voltage is 67 microvolts. Its output device was a voltage to frequency converter calibrated to 1000 Hz full scale. The manufacturer specifies the integration to be linear within .01% and reproducible to .001%. Pulses were registered on a preset counter (Digitool Corporation Model 729-2). The first pulse simultaneously started an oven-stablized 1 MHz oscillator clock (Atec, Inc. Model 6086) which was stopped by a contact closure when a preset count was reached. The irreproducibility of relay switching-time introduced less than .001% error into current measurements. Time is an inverse measure of the current. Intervals required for the measurement of ion currents varied from ca. 30 to ca. 90 seconds, and were determined with  $\pm 1$  msec. precision. Figure 3 is a block diagram of the measurement system. The entire facility was tested for linearity against a Mercury cell constant current supply (Gyra Electronics Corporation No. CS-57) which had been recently calibrated within .0025% against a secondary standard (Linear Standards Laboratory, Inc.). For currents between 1.5 and 3.0 X  $10^{-9}$  A, the departure from linearity was found to be less than .03%; all sample ion currents measured were in this range.

Before measuring the saturation current value at each pressure, the linear portion of the field dependency was determined tentatively. This is the region in which recombination of ions is reduced to within the experimental error of the line, but below the voltage minimum of the proportional region. Ion currents were measured beginning at a chosen maximum voltage, usually 2800 V, and proceeding in decrements of 100 volts to a value where current was no longer a linear function of applied voltage. The series was then reversed and continued until the maximum was reached again. The two measurements at each voltage were averaged to eliminate the effect of experimental drift upon the saturation current plot. The ion current data, usually for at least ten voltage values, were treated by a least squares adjustment to determine the intercept of the line—the saturation current at that pressure. (Appendix B). A step-wise list for collection and treatment of data is given in Appendix C.



RESULTS

#### RESULTS

#### A. Saturation Current

Two types of plots of ion current vs. voltage may be obtained, depending upon the polarity of the field applied to the chamber, as illustrated in Figure 4. A positive potential (the collecting electrode is essentially at ground) accelerates all the negatively charged species toward the chamber wall and the beta energy is enhanced by an amount proportional to the applied voltage. A plot of current vs. voltage therefore exhibits a positive slope corresponding to the rate of increase in ionization with increases in beta energy. When a negative potential is applied to the wall, beta particles are retarded, and a corresponding proportional reduction of sample current is observed. The difference in intercepts for the two polarities yields the Ni-63 activity directly as 2.6 cm while a mean energy of  $4.4 \pm .2$  keV may be calculated<sup>62</sup> for the beta particles of this radiation source.

The slope of the line is generally close to .5%/kV for the "positive" graph and ca. .3%/kV for the "negative" plot. Moreover, when the potential on the chamber is positive, beta-rays emitted from the source contribute to the total ion current, while they do not when polarity is reversed. When the chamber is evacuated one can only measure a meaningful zero current for positive HV polarity, and all measurements were therefore made in this mode. The resulting plots yield intercept values whose standard deviations are about .01% for ten data points, and as low as .005% in favorable cases. The linear portion of the graph is observed over a 1-3 kV range for most samples, with the minimum saturating voltage between 1.0 and 2.0 kV. It was found convenient to superimpose a small offset current from the current source. This "zero current" (beta current plus cell current) is measured frequently when the system is under vacuum and this value is subtracted from the intercept of the sample current (beta current plus cell current plus ion current) vs. voltage plots. The plots displayed in Figure 4 were obtained using the absolute values of the remainders, which accounts for the crossing of the lines. The zero-current subtraction also eliminates the long-term drift error of the integrator, the error due to decay of the mercury cells with age and power consumption and the day-to-day fluctuation of cell current (normally  $\leq \pm .005\%$ ) which results from changes in room temperature.

The ability to obtain ionization current measurements reproducible within .03% or less is critically dependent on the condition of the chamber walls and beta-source wires. When oxygen is introduced to the chamber for several hours the saturation current of  $N_2$  measured subsequently is reduced by several percent. The lower value of the saturation current is maintained reproducible thereafter. If  $H_2$  is later introduced and allowed to stand for several hours, subsequent measurements of  $N_2$  current are restored to approximately the original level, and continue to increase for several days.

In addition to what are presumable oxide coatings, the sample or products may adsorb or deposit on the chamber surfaces. Ionization currents in  $N_2$  taken for calibration at the end of the day are consistently lower than those measured at the beginning. This decrease is noted for sample currents as well. Therefore all measurements were corrected with respect to the difference between the first and last N2 measurements. This adjustment does not always provide a satisfactory correction for the sample currents, as the period during which such coatings are being deposited is only the interval between the introduction of the first sample and the removal of the last, and some of the coating is removed by evacuation. Also, the first  $N_2$  measurement is made after overnight evacuation, whereas the last is made after only 15 minutes of pumping. Therefore a correction was applied to the sample ion currents, assuming that the change in the values of the first and last measurement are linear with time. These corrections were typically ca. 0.05% to 0.08%, and their magnitude was dependent on the type of sample and the time elapsed from the beginning to the end of the interval. Occasionally a somewhat larger drift was observed, but all such data were rejected and are not reported here if the correction exceeded 0.1%.

It may be noted that while coatings on the chamber wall may affect the experiments by contributing contaminants to the system, the principal effect of coatings on the wires is to reduce the mean energy of beta particles. This latter type of error reduces both the nitrogen and sample currents in the same proportion and this error is self-eliminating in the ratio of sample current to  $N_2$  current at a chosen electron density reference.

The ratio of sample current to reference current is not only

reprobucible over extended periods but also affords normalized ion currents which are used to compute precise relative W-values. Since the ionization current depends to some extent on the total stopping power, which is in turn proportional to electron density for a given compound,we have chosen 6.73 X  $10^{20}$  electrons cc<sup>-1</sup> as the reference point. At room temperature this corresponds to about 1500 torr and at 200 degrees C, about 2400 torr N<sub>2</sub>. Expressing sample ion currents relative to N<sub>2</sub> ion currents also obviates the long-term error which accrues in the natural decay of the Ni-63 isotope, about .0015% per day. (Appendix D.) The amount of energy lost as a result of interception of beta particles by the wires of the grid should also depend primarily upon electron densities.

B. Dependence of Saturation Current Upon Electron Density

Ionization current measurements for most samples were conducted at least twice on non-consecutive days in order to acquire sufficient data to represent the range from the minimum to the maximum pressure. Normalized currents were reproducible to within  $\pm$  .05% or less in most cases.

Saturation currents were measured for most samples over the range from 4 to 12 X  $10^{20}$  electrons cc<sup>-1</sup>. In every case the current value was within 1% of its maximum after the electron density had reached 5 X  $10^{20}$  electrons cc<sup>-1</sup>. Figures 5-8 illustrate the behavior of N<sub>2</sub>, of all normal and branched chain alkane isomers through hexane, of n-C<sub>7</sub>H<sub>14</sub> and of argon in the range 6 to 12 X  $10^{20}$  electrons cc<sup>-1</sup>. The largest increase observed in this range was .56 ± .14% for n-heptane.

The maximum electron density obtainable in methane was only 9 X  $10^{20}$  electrons cc<sup>-1</sup> and ionization currents did not become constant within this range. Saturation currents in nitrogen and in ethane were constant to within  $\pm$  .05% for electron densities above 8 X  $10^{20}$  electrons cc<sup>-1</sup>. Beyond ca. 15 X  $10^{20}$  electrons cc<sup>-1</sup> extrapolation of plots of ionization current versus voltage became uncertain because external discharges limited the available voltage range.

The effect of temperature on relative ionization currents was investigated for methane, ethane, propane, nitrogen and argon between 23° and 200°C. Data taken at room temperature are represented by open symbols in Figures 5 and 8 while solid symbols represent data obtained at temperatures between 180°C and 200°C. No difference could be noted within the limits of accuracy provided that ionization currents are compared at equal electron densities.

C. W(beta) Determinations

Nitrogen was chosen as a reference for computation of W primarily because saturation currents in this gas are reasonably insensitive to small amounts of impurities; the gas therefore requires no additional purification or special handling.<sup>46</sup> The range of electron densities from 6 to 12 X  $10^{20}$  electrons cc<sup>-1</sup> was found to yield saturation currents which could be considered reliable and a curve was fitted to the data over that range. Saturation current values were interpolated from the graph at intervals of 1 X  $10^{20}$  electrons cc<sup>-1</sup> and the ratio of nitrogen current to sample current was multiplied by 34.6 eV, the weighted mean W for N<sub>2</sub> recommended in Whyte's 1963 review,<sup>41</sup> as well as the mean obtained in Table II. The resultant relative values of W for the normal alkanes through heptane, for all branched chain isomers through heptane and for argon are listed in Table V. The errors indicated for the measurement at 10 X  $10^{20}$  electrons cc<sup>-1</sup> (typically ca. ± 0.1%) were obtained by summing the relative standard deviations of the intercepts in the four ionization current measurements upon which the calculation was based--two for the normalized nitrogen saturation current and two for the normalized saturation current of the sample.

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## DISCUSSION

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#### DISCUSSION

## A. Evaluation of Saturation Current Measurements and Experimental Artifacts

Two conditions must be fulfilled to make W-values based on relative ionization current measurements acceptable. First, the beta particle must expend all its energy, or a reproducible fraction thereof, in the gaseous systems. Secondly, complete collection of primary ion pairs must be achieved. The first condition dictates a minimum electron density for a given chamber. The second suggests a maximum pressure above which recombination will become competitive. In order that ratios of saturation currents may be used to calculate W(beta), it must also be assumed that energy loss due to interception of beta particles by the wires of the collecting electrode is proportionately the same in different gases for equal electron densities and that enhancement of current by the effect of the field on beta energy is linear in all systems. The behavior of saturation currents reported here can be considered in terms of these conditions and with respect to the backscattering of particles by the gas.

The stopping power for electrons in a gas is proportional to pressure if the temperature is fixed. The minimum pressure used in every system was sufficient to stop beta particles of maximum energy = 66 keV within the radius of the chamber, according to calculations based on the available beta spectra of Ni-63,<sup>60,63</sup> its maximum energy<sup>59,60</sup> and the probable average energy of our source. The geometry of our collecting electrode, however, is responsible for an effect of significant magnitude. The probability of intercepting beta particles by the wires is almost 2% in the evacuated chamber (Appendix E). The amount of additional energy available to the gaseous system increases with pressure, so that enhancement of ionization is anticipated. The resultant effect upon ion current measurements will approach a limiting value as the electron density increases.

Increased ion current is also expected from the enhancement of beta energy in the electric field. Although existence of such an effect has been questioned,  $^{54}$  the following observation supports this hypothesis strongly. At low pressures the greater range of the beta particle will permit an enhanced amount of energy acquisition as the particle falls through a longer distance. At higher pressures, the shorter path causes the beta particle to lose most of its energy very near the electrode, and the rest of the acceleration is exerted on the remaining subexcitation electron. This effect therefore causes the ion current to approach an upper limit asymptotically as pressure increases. The positive slope of the ion current vs. voltage plot decreases hyperbolically with pressure, and the regularity of this decrease can be employed as a criterion for collection completeness.  $^{64}$ 

At sufficiently high pressures recombination prevents complete collection and measured intercepts will be too low. This well-known characteristic of incomplete collection may be correlated with ionization chamber theory.<sup>65</sup> Collection efficiency (f) for an approximately spherical chamber containing a given gas may be expressed as the positive root of a quadratic equation, reduced to a function of pressure (P) and applied field (V):

$$f = \frac{-1 + [1 + 4 k (P/V^2)]^{1/2}}{2 k (P/V^2)}$$

Approximations appropriate to the recombination of the gas in the chamber are included in the constant k, namely the coefficient of recombination, ionic mobilities and intensity of ionization in the gas, and the radii of the chamber and its collecting electrode. The collection efficiency should be essentially unity at low pressures and high voltages, but the above equation predicts that as the applied potential is reduced from 3.0 to 1.0 kV, the loss of ion current in nitrogen at 3200 torr will be twice that expected at 1600 torr. (A calculation of collection efficiency is given in Appendix F.) The resulting increase in the slope of the ion current versus voltage plot is accompanied by a decrease in the measured intercept as pressure increases. This is a necessary test for the acceptability of data at high pressures, but the absence of this effect in the range of electron densities studied indicates that recombination was not competitive, and the good linearity with voltage of the saturation current plots indicates that the collection efficiency is essentially unity.

Another important consideration is the backscattering of beta particles from the gas to the grid wires. Jesse has demonstrated that with certain source geometries this phenomenon can cause sizeable decreases in ion current.<sup>66</sup> Energy loss increases with pressure and with effective atomic number  $(\Sigma Z_i^2) / (\Sigma Z_i)$  of the gas. By using small diameter wires, with large spacing between them and a large distance between the source area and the ring upon which the wires are mounted, backscatter can be essentially eliminated even at pressures as high as 6000 torr.<sup>54</sup> The effective atomic numbers varied only between 4.0 and 4.6 for the alkanes while those of nitrogen and argon are 7 and 18, respectively. There is no corresponding systematic change in the behavior of the gases studied in this work, and the error introduced by scattering is considered to be small relative to the ±.1% error of W - measurements.

#### B. Evaluation of W(beta) Determinations

Applying the above considerations to the gases studied, acceptable results were obtained over the range of electron densities from 6 to 12  $\times 10^{20}$  electrons cc<sup>-1</sup>. Above the upper limit of this range the effects of recombination and/or backscatter become evident and therefore no

valid results at these higher pressures were obtained.

At pressures above one atmosphere, the collision-free period in a gas becomes less than  $10^{-10}$  seconds and bimolecular events become significant.<sup>1</sup> Since both ionization and dissociation may be induced by collision, it is of interest whether the competition between the two processes is temperature and pressure dependent.

Processes which might inhibit ionization at elevated pressures include recombination and collisional deactivation of excited neutrals (superexcited states, autoionizing states and preionizing states).<sup>13,67</sup> On the other hand, ionization may be enhanced by associative (Hornbeck-Molnar) ionization resulting in a singly charged dimer or by non-associative processes, in which a highly energetic secondary electron or neutral molecule induces ion pair formation upon collision with a second neutral.

Chemical effects would not be unexpected in a temperature increase from 25°C to 200°C, since several tenths of an eV are gained by vibrational modes. Several samples  $(N_2, CH_4, C_2H_6, C_3H_8, C_4H_{10})$  were studied at room temperature and at 200°C. In no case was a temperature dependency noted.

For most samples, no pressure dependency is exhibited for W(beta) in the density range 6 to 12 X  $10^{20}$  electrons cc<sup>-1</sup>. For argon and n-butane, however, the change was sufficiently large with respect to the uncertainty that a decrease seems possible. In each case the change was ca.  $.3\% \pm .2\%$ . Such a decrease in W would have to be attributed to chemical effects since the physical causes for enhanced ionization have been incorporated into the computed W. The increase in W for argon between 6 and 10 X  $10^{20}$ 

electrons cc<sup>-1</sup> is probably attributable to the backscatter effect discussed earlier. In both cases the magnitude of the change is barely larger than experimental uncertainty.

C. Comparison of Results to Reports of Previous Workers

The values of W(beta) measured in this work at 10  $\times$  10<sup>20</sup> electrons cc<sup>-1</sup> electron density provide the most complete list currently available for alkane isomers. Considering the large discrepancies among the values previously reported for some of these compounds and for argon, and in view of the wide variety of experimental conditions used, meaningful comparisons are difficult. However, the work of Jesse<sup>54</sup> and Jesse and Sadauskis<sup>22,46</sup> is highly respected because of their attention to experimental accuracy and precision and, when necessary, to the purity of gases. The argon W-value measured here is in good agreement with Jesse's recommended value of 26.38 eV.<sup>19</sup> His measured W's for methane and ethane were ca. 1% higher than those of this work, which is consistent with our having chosen a reference W-value for nitrogen which was about 1% lower than his measured value, for reasons explained earlier. Adler and Bothe, whose results include the backscatter correction recommended by Jesse,  $^{66}$  have conducted extensive studies of W (beta) for organic systems.<sup>23</sup> Their experimental design is quite similar to that of Jesse and to that used in this research except for the source geometry. The values they report are consistently at least 1% higher than our own,

which may be partly attributable to their choice of 33.8 eV as the reference W-value for air, a value slightly higher than that recommended by Whyte.<sup>41</sup>

D. Energy Balance Parameters

Adler and Bothe calculated the relative amounts of energy deposited in ionization, excitation and the scattering of subexcitation electrons, based upon the previously mentioned energy balance equation.<sup>23</sup> The mean energies of ions were determined from mass spectrometric data according to Stevenson's formula<sup>68</sup>

$$\overline{E}_{i} = \frac{\Sigma f_{i}^{A} i}{\Sigma f_{i}},$$

where  $f_i$  is the ion intensity and  $A_i$  its appearance potential. Mean energies of subexcitation electrons were calculated from the lowest excited state energies ( $E_0$ ) and ionization potentials ( $I_0$ ) by the equation of ElKomoss and Magee<sup>69</sup>

$$\overline{E}_{se} = \frac{E_0}{2 + E_0 / I_0}$$

The quantity  $(N_x/N_i\overline{E}_x)$  was then obtained by difference between measured W's and the sum of  $\overline{E}_i$  and  $\overline{E}_{se}$ . For methane, ethane, propane and n-butane, the relative amounts of energy expended in ionization, excitation and remaining in subexcitation electrons were reported to be  $53\pm2\%$ ,  $34\pm2\%$  and 13%, respectively. Chen has calculated average energies of ions employing a modification of Stevenson's formula<sup>70</sup> so that the process which occurs at the next energy level (AP<sub>n</sub>) above the ionization threshold is also considered:

$$\overline{E_{i}} = \frac{\frac{1}{2} \sum_{i=1}^{n-1} f_{i} (AP_{i} + AP_{i+1}) + f_{n} AP_{n}}{\sum_{i=1}^{n} f_{i}}$$

Using the W-values of this work, the relative amounts of deposited energy within this series (Table VI) varies slightly less than those reported by Adler and Bothe but are in excellent agreement with their work. For the normal alkanes from  $C_1$  through  $C_5$ , the relative amounts of energy expended are 12.1 ±.2% in subexcitation electrons, 54.5 ±1.1% in ions and 33.4±.8 in excited neutral species.

#### E. Correlation with Molecular Structure

Values of W, Ionization Potential  $(I_0)$  and W/I<sub>0</sub> are listed in Tables VII through IX as functions of chain length and degree of methyl substitution. Both W and I<sub>0</sub> decrease with increasing methylation on a given chain length. Among the isomers of a particular compound, W's increase while ionization potentials decrease with increasing substitution. This effects a marked increase in W/I<sub>o</sub> with increasing methylation among isomers. This quantity also increases with increasing chain length and

with increasing methylation of a given chain length, as is expected because of the additional vibrational modes available.

The results of these correlations may be applied to the prediction of W's for compounds not yet investigated. As the chain length and the degree of substitution increase, the amount by which W decreases and  $W/I_0$ increases becomes smaller. Applying these considerations and using known ionization potentials,<sup>71</sup> W and  $I_0$  may be predicted within ± .1 eV for other alkane isomers. The systematic changes in W, $I_0$  and  $W/I_0$  observed with increasing chain length, number of methyl groups and number of carbon atoms are extrapolated, maintaining self-consistency among the three tables. Estimated values for several heptane isomers and n-octane are included in parentheses in the tables.

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## CONCLUSIONS
#### CONCLUSIONS

W(beta) values for alkanes relative to that of nitrogen can be measured with a precision of 0.1% provided that certain corrections are applied and that comparison is made at equal stopping powers as approximated by electron densities. W(beta) for argon can be determined to within 0.2%. Within experimental uncertainty, normal alkanes through heptane, branched isomers through hexane and argon exhibit no variation of W(beta) as pressures are increased by a factor of two, up to 2700 torr. There is also no temperature dependency of W(beta) for argon, methane, ethane and propane in the 25°-200°C range.

Energy balance considerations reveal that at least half of the energy absorbed in the complete stopping of electrons in vapors of normal alkanes  $C_1$  to  $C_5$  is expended in ionization, while about one third goes into excitation and the rest remains in subexcitation electrons.

W(beta) correlates well with molecular structure in the normal and branched alkanes. Ionization potentials  $(I_0)$  as well as W's may be predicted empirically by extrapolating values from tables of W,  $I_0$ , and W/I<sub>0</sub>.

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LITERATII

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# LITERATURE CITED

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# FIGURES

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Figure 1.

· IONIZATION CHAMBER



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### Figure 2.

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OVEN WITH GAS HANDLING SYSTEM AND

#### VACUUM SYSTEM

PT: Pressure Transducer
CC: Cold Cathode Vacuum Gauge
IC: Ionization Chamber
TC: Thermocouple-type Pressure Gauge
T: Trap
DP: Diffusion Pump

MP: Mechanical Pump



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# Figure 3.

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# Electronics

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Ion Current Measurement



#### Figure 4.

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Saturation currents in  $N_2$  at 2400 torr with positive and negative potential applied to wall (Absolute value after zero current subtraction). Dashed line is extrapolated portion. Difference between intercepts represents current due to beta particles only.



Applied Field (kV)

### Figure 5

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Dependence of saturation current on electron density for nitrogen  $\odot$ , methane  $\Box$ , ethane  $\odot$  and propane  $\Delta$ . Open symbols represent room temperature data. Solid symbols represent data obtained between 180° and 200°C.



Figure 6.

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Dependence of saturation current on electron density for n-butane  $\odot$  , n-pentane  $\Box$  , n-hexane  $\odot$  and n-heptane  $\triangle$  .



Ionization Current (arbitrary units)

### Figure 7.

Dependence of saturation current on electron density 2-methylpropane  $\odot$ , 2-methylbutane  $\square$ , 2-methylpentane  $\bigcirc$ and 3-methylpentane  $\triangle$ .

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#### Figure 8.

Dependence of saturation current on electron density for 2,2-dimethylpropane  $\square$ , 2,2-dimethylbutane  $\bigcirc$ , 2,3-dimethylbutane  $\triangle$  and argon  $\bigcirc$ . Open symbols represent room temperature data. Solid symbols represent data obtained between 180° and 200°C.



Ionization Current (arbitrary units)

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# TABLES

### Table I.

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Experimental Conditions of W(beta) Studies

n.o.: no others in literature

n.g.: not given by author

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n.a.: not available in reference

Investigator	Chamber and Radiation Source	Pressure	Temp.	Magnitude of values relative to others	Ref.
Barber 1955	Copper cylinder with mylar windows. Parallel plate electrodes. Faraday Cup detector. Linear Accelerator 1-35 MeV electrons. Collimated beam 1/2" x 1/8".	<u>&gt;</u> 760 torr	n.g.	greater	3
Jesse and Sadauskis 1955	Brass cylinder, 9 1/2 cm diam, 7 cm long H-3 on wire mesh, 3-5 keV β. C-14 β-rays Ni-63 on wire mesh, β-rays <u>&lt;</u> 20 k	n.g. eV	n.g.	approx. equal to	22,46
Weiss and Bernstein 1955,1956	Parallel plate extrapolation chamber (.475 cm spacing). Polystyrene plates coated with Aquadag. van de Graaff generator. X-rays (assumed 1 MeV) (gold target).	1956: 50 torr 1955: norma- lized to STP	n.g.	less than or equal to	50,51

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Investigator	Chamber and Radiation Source	Pressure	Temp	Magnitude of values relative to others	Ref.
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Kunz,Gross and Failla 1956	Geometry n.a. Ni-63 beta-rays and S-35 beta-rays	n.g.	n.g.	greater	55
Jesse a <b>nd</b> Sadauskis 1957	Brass cylinder 20.5 cm diam. 21.0 cm. long. Collecting electrode: Copper grid on brass ring. S-35 beta-rays.	1620 torr	n.g.	approx. equal to	22,46
Bay,Mann, Seliger and Wyckoff 1957	Long twin cylinders. Aluminum free-air ionization chamber. S-35 on collodion film sup- ported on 2" diam. tungsten loop; E <sub>max</sub> = 50keV.	n.g.	n.g.	approx. equal to	52
Wingate, Gross and Failla 1958	5 1/2" diam. copper sphere 1/16" diam. Ni rod. Ni-63 beta- rays. Source plated on tip of collecting electrode.	5-30 psi	100°C	no others	56

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Investigator	Chamber and Radiation Source	Pressure	Temp.	Magnitude of values relative to others	Ref.
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Hardwick 1958	Chamber n.g. H-3 beta-rays	n.g.	n.g.	greater	53
Jesse 1958	Brass cylinder 10.0 cm. long and 9.4 cm. diam. (all walls in field). S-35 beta on plastic film supported on brass ring mounted on collecting electrode.	1000- 6000 torr	n.g.	approx. equal to	54
Markus 1959	151 cc parallel plate chamber. 14.8 MeV electrons (Betatron).	l atm	0°C	smaller	47
Booz and Ebert 1962 1961	Free air ionization chamber 16 cm. radius with collecting electrode offset from center. 100-300 keV X-rays.	n.g.	20°C- 140°C	greater	25,26
Koepp,Booz and Ebert 1964	Parallel plate chamber. 55 keV X-rays.	l atm.	n.g.	smaller	57

Investigator	Chamber and Radiation Source	Pressure	Temp.	Magnitude of values relative to others	Ref.
Meisels 1964	Two consecutive pyrex cylinders 4.11 cm. ID and 2.05 cm. long with aluminum windows. 1 MeV electrons from van de Graaff generator.	400-700	23°C	smaller	5
Adler and Bothe 1965	Ni-63 beta -rays plated on surface of cylindrical collecting electrode	n.g.	150°	greater	23
Davidow and Armstrong 1966	Parallel stainless steel plates, 2 cm teflon cylinder, 6 cm diam. Co-60 γ- rays.	100-700 torr	n.g.	no others	30
LeBlanc and Herman 1966	155 ml. cylinder, 46 mm diam. Pyrex, with graphite coating. Co-60 γ- rays	150-400 torr	n.g.	smaller	38

Investigator	Chamber and Radiation Source	Pressure	Temp.	Magnitude of values relative to others	Ref.			
Buktas 1967	n.g. H-3 (β), Ē <sub>β</sub> = 3.3 keV plate mounted	160 torr	20°C	greater	28			
Cooper and Mooring 1968	Pyrex cylinder coated with silver. Cylindrical field. Co-60 <del>y</del> -rays. E not given.	300-800 torr	n.g.	greater	29			

# Table II.

Values of W(beta) reported for nitrogen, argon and several alkanes.

### References:

a)	Cooper and Mooring, 1968, Co-60 gamma-rays	29
b)	Büktas, 1967, H-3 beta-rays	28
c)	LeBlanc and Herman, 1966, Co-60 gamma-rays	38
d)	Adler and Bothe, 1965, Ni-63 beta-rays	23
e)	Koepp, Ebert and Booz, 1964, 55 keV X-rays	57
f)	Meisels, 1964, 1 MeV electrons	5
g)	Booz and Ebert, 1961 and 1962, .13 MeV X-rays	25,26
h)	Markus, 1959, 14.8 MeV electrons	47
i)	Jesse, 1958, S-35 beta-rays	54
j)	Hardwick, 1958, H-3 beta-rays	53
k)	Kunz, Gross and Failla, 1956, Ni-63 and S-35 beta-rays	55
1)	Jesse and Sadauskis, 1955, 1957, Ni-63, S-35, C-14 and	
	H-3 beta-rays	22,46
m)	Weiss and Bernstein, 1955 and 1956, X-rays	50,51
n)	Barber, 1955, 1-35 MeV electrons	3

							W(b	eta) (	eV)				•	ŗ		
Sample	a	b	с	d	е	f	g	h	i	j	k	1	m	n	Mean	Av. Dev.
сн <sub>4</sub> .			27.6	27.5		26.7	29.9	25.1	27.3	27.6	27.6		26.8		27.3	.7
<sup>C</sup> 2 <sup>H</sup> 6	25.4		24.6	26.0		23.6	26.5		24.5			24.8			25.1	. 8
с <sub>3</sub> н <sub>8</sub>	24.9		23.5	24.3		23.4	26.2								24.5	.8
<sup>n-C</sup> 4 <sup>H</sup> 10	24.1		22.9	23.7		22.9									23.4	.5
n-C <sub>5</sub> H <sub>12</sub>				23.5	20.5										22.0	1.5
<sup>n-C</sup> 6 <sup>H</sup> 14				23.4											23.4	
n-C7 <sup>H</sup> 16				23.2											23.2	
i-C4 <sup>H</sup> 10	24.6		23.4			23.0			2						23.7	.6
i-C <sub>5</sub> H <sub>12</sub>					21.0	23.9									22.4	1.4
neo-C5 <sup>H</sup> 12			23.2								·				23.2	
<sup>N</sup> 2		35.20		34.9		34.1	34.6	32.3	34.8	35.0	35.0	35.0	34.6	34.8	34.6	.5
Ar		27.29	25.7				23.6					26.4	25.8		25.8	.9

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# Table III.

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# Record of Samples Used in W(beta) Measurements.

Sample	Supplier	Grade Specif	ied Purities (%)
Nitrogen	Iweco, Inc.	High Purity Dry	99.995
Nitrogen	Matheson Gas Products	Research Grade	99.9995
Methane	Matheson Gas Products	Research Grade	99.9
Ethane	Phillips Petroleum Co.	Research Grade	99.9
Propane	Matheson Gas Products Co.	Chemically Pure Grade	99
n-butane	Air Products and Chemicals Co.	Instrument Grade	99
n-butane	Matheson Gas Products Co.	Instrument Grade	99
n-pentane	Phillips Petroleum Co.	Research Grade	99 <b>.</b> 9
n-hexane	Phillips Petroleum Co.	Research Grade	99.9
n-heptane	Fisher Scientific Co.	Certified Spectranalyzed	
2-methylpropane	Air Products and Chemicals Co.	Instrument Grade	99
2-methylbutane	Phillips Petroleum Co.	Research Grade	99.9
2-methylpentane	Phillips Petroleum Co.	Research Grade	99.9
3-methylpentane	Phillips Petroleum Co.	Research Grade	99
2,2-dimethylpropane	Matheson Gas Products Co.	Chemically Pure Grade	99
2,2-dimethylbutane	Phillips Petroleum Co.	Pure Grade	99
2,3-dimethylbutane	Phillips Petroleum Co.	Pure Grade	99
Argon	Matheson Gas Products Co.	Research Grade	99.9995

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# Table IV.

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Interpolated Saturation Currents for Some Alkanes, Nitrogen and Argon.

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	Tomzacion, current, (Arbitrary, onits)								
		El	ectron Density	(electrons cc	<sup>-1</sup> x 10 <sup>-20</sup> )				
Gas	6.0	7.0	8.0	9.0	10.0	11.0	12.0		
сн <sub>4</sub>	1.2819±.0059	1.2842±.0036	1.2855±.0048	1.2858±.0036	1.2867±.0036				
с <sub>2</sub> н <sub>6</sub>	1.4310 ±.0002	1.4315 ±.0002	1.4320 ±.0002	1.4324±.0002	1.4327±.0002	1.4323#.0002	1.4325±.0002		
с <sub>3</sub> н <sub>8</sub>	1.4603±.0011	1.4616±.0011	1.4624±.0011	1.4628±.0011	1.4625±.0011	1.4620±.0029	1.4614±.0029		
n-C <sub>4</sub> H <sub>10</sub>	1.4884±.0007	1.4910±.0007	1.4928±.0007	1.4944±.0007	1.4956±.0007	1.4964±.0007	1.4966±.0007		
n-C <sub>5</sub> H <sub>12</sub>	1.5128±.0008	1.5154±.0008	1.5172±.0008	1.5184±.0007	1.5195±.0007	1.5198±.0007	1.5196±.0007		
n-C <sub>6</sub> H <sub>14</sub>	1.5274±.0009	1.5290±.0009	1.5300±.0009	1.5310±.0009	1.5320±.0009	1.5328±.0009	1.5333±.0009		
n-C <sub>7</sub> H <sub>16</sub>	1.5355±.0008	1.5386±.0008	1.5416±.0014	1.5426±.0014	1.5434±.0014	1.5442±.0014	1.5435±.0009		
i-C <sub>4</sub> H <sub>10</sub>				1.4738±.0002	1.4743±.0002	1.4744±.0002	1.4725±.0002		
i-C <sub>5</sub> H <sub>12</sub>	1.4986±.0013	1.4994±.0013	1.5000±.0013	1.5008±.0013	1.5016±.0013	1.5023±.0013	1.5031±.0013		
i-C <sub>6</sub> H <sub>14</sub>					1.5205±.0007	1.5198±.0014	1.5188±.0014		
3-methy1-C <sub>5</sub> H <sub>12</sub>					1.5282±.0003	1.5281±.0003	1.5279±.0003		
neo-C <sub>5</sub> H <sub>12</sub>	1.4752±.0008	1.4773±.0008	1.4788±.0008	1.4796±.0008	1.4805±.0008	1.4810±.0008	1.4808±.0008		
neo-C <sub>6</sub> H <sub>14</sub>			1.5128±.0002	1.5133±.0002	1.5138±.0002	1.5144±.0002	1.5150±.0002		
2,3-dimethy1-C <sub>4</sub> H <sub>10</sub>	, ·	1.5160±.0002	1.5172±.0002	1.5184±.0002	1.5191±.0002	1.5189±.0002	1.5185±.0003		
N <sub>2</sub>	.9989±.0005	1.0003±.0004	1.0012±.0010	1.0012±.0005	1.0012±.0007	1.0012±.0007	].0012±.0008		
Ar	1.314 ±.003	1,314 ±.003	1.314 ±.003	1.313 ±.003	$1.311 \pm .003$	1.309 ±.003			

Ionization Current (Arbitrary Units)

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Table V.

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W(beta) in eV for Alkanes and Argon Relative to W = 34.6 eV for Nitrogen.

		Electron	Density	(electron:	s cc-1 x 10-20)			Ref 40	Table II
Sample	6.0	7.0	8.0	9.0	10.0	11.0	12.0	Weighted Mean	Mean
methane	26.96	26.95	26.95	26.94	26.92 ±.09			27.3	27.3
ethane	24.15	24.18	24.19	24.19	24.18±.02	24.18	24.18	24.6	25.1
propane	23.67	23.68	23.69	23.68	23.69±.03	23.70	23.71		24.5
n-butane	23.22	23.21	23.21	23.18	23.16±.03	23.15	23.15		23.4
n-pentane	22.85	22.84	22.83	22.82	22.80±.03	22.80	22.80		22.0
n-hexane	22.63	22.64	22.64	22.63	22.61±.03	22.60	22.59		23.4
n-heptane	22.51	22.49	22.47	22.46	22.45±.04	22.43	22.44		23.2
2-methylpropane				23.51	23.50±.02	23.50	23.53		23.7
2-methylbutane	23.06	23.08	23.10	23.08	23.07±.04	23.06	23.05		22.4
2-methylpentane					22.78±.03	22.79	22.81		
3-methylpentane					22.67±.02	22.67	22.67		
2,2-dimethylpropane	23.43	23.43	23.43	23.41	23.40±.03	23.39	23.40		23.2
2,2-dimethylbutane			22.90	22.89	22.88±.02	22.88	22.87		
2,3-dimethylbutane		22.83	22.83	22.82	22.80±.02	22.81	22.81		
argon	26.30	26.34	26.36	26.38	26.42±.05	26 <b>.</b> 47		26.2	25.9 44

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## Table VI.

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Energy Balance parameters for normal alkanes: methane through n-pentane

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Gas	W(ev)	Ē <sub>se</sub> (ev)	Ē <sub>i</sub> (ev)	$\overline{E}_{se} + \overline{E}_{i}$	(N <sub>x</sub> /N <sub>i</sub> )Ē <sub>x</sub> (ev)	Ē <sub>se</sub> /W(%)		Ē <sub>i</sub> /W(%)		$(N_x/N_i)\overline{E}_x/W(\%)$	
	a	b	с		d	е	f	е	f	е	f
CH <sub>4</sub>	26.92	3.3	14.6	17.9	9.0	12.3	13	54.2	54	33.5	33
<sup>C</sup> 2 <sup>H</sup> 6	24.18	2.9	13.5	16.4	7.8	12.0	13	55.8	56	32.2	31
<sup>С</sup> з <sup>Н</sup> 8	23.69	2.8	13.3	16.1	7.6	11.8	13	56.1	51	32.1	36
n-C <sub>4</sub> H <sub>10</sub>	23.16	2.8	12.4	15.2	8.0	12.1	13	53.5	51	34.4	36
n-C <sub>5</sub> H <sub>12</sub>	22.80	2.8	12.1	14.9	7.9	12.3		53.1		34.6	
1ean	a) This b) Mean ElKo c) Mean	work. W(beta) energy of subex moss and Magee. energy of ions	at 10 x 10 <sup>20</sup> citation ele 69 calculated 1	<sup>)</sup> electrons co ectrons calcul by Chen <sup>70</sup> fro	-1. ated by Chen <sup>70</sup> 1 om a modificatior	12.1±.2 from the	13 . formu	54.5 la of la of S	±1.53± Steven	2 33.4±.8 son. <sup>68</sup>	34±2
	d) W mi	nus $(\overline{E}_{so} + \overline{E}_{i})$	•								
	e) This	work combined w	ith that of	Chen. 70							
	f) Adle	er and Bothe. $^{23}$									
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### Table VII.

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Correlation of W(beta) to Chain Length and Degree of Methyl Substitution. Values in Parentheses are estimated.

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	Number		Chain Length									
Substitution	groups	1	2	3	4	5	6	7	8			
None	1	26.92										
None	2		24.18	23.69	23.16	22.80	22.61	22.45	(22.36)			
2-CH <sub>3</sub>	3			23.50	23.07	22.78	(22.58)	(22.44)				
з-сн <sub>з</sub>	3				23.07	22.67	(22.52)	(22.38)				
2,2-di-CH <sub>3</sub>	4			23.40	22.88	(22.60)						
2,3-di-CH <sub>3</sub>	4				22.80	(22.59)						
2,2,4-tri-CH <sub>3</sub>	5				(22.65)							

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#### Table VIII.

Correlation of Ionization Potential  $(I_0)$  to Chain Length and Degree of Methyl Substitution.

\*A. J. C. Nicholson, J. Chem. Phys. <u>43</u> 1171 (1965)<sup>†</sup>

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<sup>TC</sup>Theoretical Calculation, C. E. Melton and H. W. Joy, Can. J. Chem. <u>44</u>1455 (1966)<sup>+</sup>

- All Other Values: K. Watanabe, T. Nakayama and J. Mottl, J. Quant. Spectrosc. Radiat. Transfer <u>2</u> 369 (1962)<sup>†</sup>
- <sup>†</sup>in J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl and F. H. Field, <u>Ionization Potentials, Appearance</u> <u>Potentials and Heats of Formation of Gaseous Positive Ions</u>, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.) 26 (1969)

Values in parentheses are estimated (This work).

								•	
Type of	Number of mothul				Chain Le	ngth			·····
Substitution	groups	1	2	3	4	5	6	7	8
	1	12.70*							
None	2		11.52*	11.07	10.63	10.35	10.18	10.08	10.03 <sup>TC</sup>
.2-CH <sub>3</sub>	3			10.57	10.32	10.12	(0, 00)		
3-CH <sub>3</sub>	3					10.08	(9.98)		
2,2-di-CH <sub>3</sub>	4			10.35	10.06	(0,00)			
2,3-di-CH <sub>3</sub>	4				10.02	(9.89)			
2,2,4-tri-CH <sub>3</sub>	5					9.86			

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## Table IX.

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Correlation of W(beta) /  $I_{_{\scriptsize O}}$  to Chain Length and Degree of Methyl Substitution.

Values in Parentheses are Estimated.

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Type of	Number of methy	1		<u> </u>					
Substitution	groups	<b>`</b> ]	2	3	4	5	6	7	8
					<u></u>	<del></del>			<u></u>
	1	2.12	•						
None	2		2.10	2.14	2.18	2.20	2.22	2.23	(2.24)
2-CH3	3			2.22	2.24	2.25	(0.00)	(2.07)	
3-CH <sub>3</sub>	3					2.25	(2.20)	(2.27)	
2,2-di-CH <sub>3</sub>	4		•	2.26	2.27	(2.20)			
2,3-di-CH <sub>3</sub>	4				2.28	(2.28)			
2,2,4-tri-CH <sub>3</sub>	5								

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# APPENDIXES

#### A. Electron Density Calculation: Solution to van der Waals' Equation

For one mole of a real gas: 
$$(P + \frac{a}{v^2}) \cdot (V-b) = RT$$
  
 $P = \text{pressure (atmospheres)}$   $V = \text{molar volume (liter/mole)}$   
 $T = \text{temperature (Kelvin)}$   $R = .08206 \text{ liter} \cdot \text{atm./mole} \cdot \text{deg.}$   
Van der Waals constants: attractive:  $a(\frac{(\text{liters})^2 \text{ atm}}{(\text{mole})^2})$   
 $compressibility: b(\frac{\text{liters}}{\text{mole}})$ 

Rearrange for solution of equation cubic in V

$$V^{3} + (-b - \frac{RT}{P}) V^{2} + (\frac{a}{P})V + (-\frac{ab}{P}) = 0$$
  
Let  $V = X - \frac{p^{*}}{3}$ ;  $p^{*} = (-b - \frac{RT}{P})$ ;  $q^{*} = (\frac{a}{P})$ ;  $r^{*} = (-\frac{ab}{P})$   
Also let  $a^{*} = \frac{1}{3}(3q^{*} - p^{*2})$  and  $b^{*} = \frac{1}{27}(2p^{*3} - 2p^{*}q^{*} + 27r^{*})$   
And let  $A = [-\frac{b^{*}}{2} + (\frac{b^{*2}}{4} + \frac{a^{*3}}{27})^{1/2}]^{1/3}$   
and  $B = [-\frac{b^{*}}{2} - (\frac{b^{*2}}{4} - \frac{a^{*3}}{27})^{1/2}]^{1/3}$ 

The non-extraneous solution is

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$$V = A + B - \frac{p^*}{3}$$

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Given the Molecular Weight: Density =  $\frac{Mol. Wt.}{Molar Volume}$ Given the Atomic No.: Electron Density = Density X  $\frac{At. No. X Avag. No.}{Mol. Wt.}$ 

> or Electron Density = <u>At. No. X Avag. No.</u> Molar Volume

Electron Density Calculation: Computer Program

```
, TOM STONEHAM
JOB
LIMIT (EJECT, 3), (L0, 200)
ASSIGN F:5, (DEVICE, SI)
ASSIGN F:6, (DEVICE, LO)
FORTRANH GO,LS
С
    ELECTRON DENSITY CALCULATED FROM VAN DER WAALS' EQUATION
    DIMENSION PSAMP(100), TSAMP(100), VMOL(100), WMOL(100),
   *
               AVAN(100), BVAN(100), PTRANS(100), QTRANS(100),
   *
               RTRANS(100), BEQ(100), AEQ(100), BROOT(100),
   *
               AR00T(100), DENS(100), TITLE(100), AN(100),
   *
               EDENS(100)
1
    CONTINUE
    READ (5,2) TITLE(I), I=1.20
2
    FORMAT (20A4)
    READ (5,3) N
    FORMAT (15)
3
    IF (N)8,8,4
4
    CONTINUE
    READ (5,5) (PSAMP(I),TSAMP(I),WMOL(I),AVAN(I),BVAN(I),
               AN(I), I=1, N
5
    FORMAT (6F10.0)
    R=0.08206
    DO 6 I=1,N
    PTRANS(I)=(-1.)*(BVAN(I)+R*TSAMP(I)*760./PSAMP(I))
    OTRANS(I) = AVAN(I) * 760. / PSAMP(I)
    RTRANS(I) = (-1.)*(AVAN(I)*BVAN(I)*760./PSAMP(I))
    AEQ(I)=(3.*QTRANS(I)-PTRANS(I)**2.)/3
    BEQ(I)=((2.*PTRANS(I)**3.)-(9.*PTRANS(I)*QTRANS(I))
               +27.*RTRANS(I))/27.
    AROOT(I)=((BEQ(I)/(-2.))+SQRT((BEQ(I)**2.)/4.+(AEQ(I)
                **3.)/27.))**(1./3.)
    BROOT(I) = ((BEQ(I)/(-2.)) - SQRT((BEQ(I)**2.)/4.+(AEQ(I)))
   *
                **3.)/27.))**(1./3.)
    VMOL(I) = AROOT(I) + BROOT(I) - (BVAN(I) + (R*TSAMP(I)*(760.))
               /PSAMP(I)))/3.
    DENS(I)=WMOL(I)/VMOL(I)
    EDENS(I) = AN(I) / WMOL(I) * DENS(I) * (6.025)
6
    CONTINUE
    WRITE (6,7) (TITLE(I), I=1,20), N, (PSAMP(I), TSAMP(I),
   *
               WMOL(I),AVAN(I),BVAN(I),VMOL(I),DENS(I),
   *
               AN(I), EDENS(I), I=1, N
    FORMAT (1H1,///
7
             5X,20A4,///,5X,'N=',I5,//,3X,'PRESSURE',3X
   *
             'TEMPERATURE',3X,'MOL. WT.',5X,'A',9X,'B',
5X,'MOLAR VOL.',5X,
'DENSITY',4X,'AT. NO.',4X,"ELECT.DENS.*10**
   *
   *
   *
               -20',//(9(1X,1PE11.4)))
   *
     GO TO 1
     CONTINUE
8
     STOP
     END
```

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B. Computer Program for Least Squares Adjustment

```
,TOM STONEHAM
JOB
LIMIT (EJECT, 3), (L0, 200)
ASSIGN F:5, (DEVICE, SI)
ASSIGN F:6, (DEVICE, LO)
FORTRANH GO, LS
     LEAST SQUARES TREATMENT FOR PARAMETERS OF ANY LINE
С
     DIMENSION X(100), Y(100), DEV(100), TITLE(100), R(100),
    *
           RABS(100)
 3
     CONTINUE
     READ (5,1) TITLE(I), I=1,20
     FORMAT (20A4)
 1
     READ (5,92) N
FORMAT (15)
92
     IF (N)93,93,2
' 2
     CONTINUE
     READ (5,91) (X(I),Y(I),I=1,N)
91
     FORMAT (2F10.0)
     KKK=IFIX(.9*FLOAT(N))
 8
     CONTINUE
     SUMA=0.
     SUMB=0.
     SUMC=0.
     SUMD=0.
     DO 5 I=1.N
      SUMA = SUMA + X(I)
     SUMB=SUMB + \chi(I)**2
     SUMC=SUMC + \hat{X}(\hat{I}) * Y(\hat{I})
 5
     SUMD = SUMD + Y(I)
     AN=N
      D=AN*SUMB-SUMA**2
     BINT=(SUMB*SUMD-SUMA*SUMC)/D
      SLOP=(AN*SUMC-SUMA*SUMD)/D
      SUME=0.
      SUMF=0.
      DO 10 I=1,N
        R(I)=Y(I)-BINT-SLOP*X(I)
      DEV(I) = SORT(R(I) * * 2)
      SUMF=SUMF+DEV(I)
      SUME=SUME+(Y(I)-BINT-SLOP*X(I))**2
10
      AD=SUMF/AN
      RAD=AD/BINT
      SD=SQRT(SUME/(AN-2.))
      SLER=SD*SORT(AN/D)
      BINER=SD*SQRT(SUMB/D)
      RELD = BINER/BINT
      RDS=SLER/SLOP
      WRITE (6,89) (TITLE(I), I=1,20),N,
     *
           (X(I), Y(I), R(I), I=1, N)
```

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```
89 FORMAT (1H1,///,10X,20A4,//,9X,'N =',15,///,9X,'X',
         13X, 'Y', 10X, 'RESIDUAL', //, 100(5X, 3(F10.5, 5X),
   *
          1))
    WRITE (6,88) AD, RAD, SD, BINT, BINER, RELD, SLOP, SLER, RDS
88 FORMAT ( //,31X,'AV DEV =',F10.5,16X,'REL AV DEV ='
            F10.6,//,31X,'STD DEV =',F10.5//,5X,'INTERCEPT
   *
          =',F10.5,5X,'STD DEV INTERCEPT =',F10.6,5X,'REL
   *
          DEV INTERCEPT =',F10.6,//,5X,'SLOPE =',F10.5,9X
'STD DEV SLOPE =',F10.6,9X,'REL DEV SLOPE =',
   *
   *
   *
          F10.6,////)
    J=0
    DO 9 I=1,N
    RABS(I) = ABS(R(I))
 9 CONTINUE
    RMAX=RABS(1)
    DO 13 I=1,N
    IF (RMAX.LT.RABS(I)) RMAX=RABS(I)
13 CONTINUE
    DO 12 I=1,N
    IF (RMAX.EQ.RABS(I)) GO TO 11
    J=J+]
    X(J)=X(I)
    Y(J)=Y(I)
    R(J) = R(I)
    DEV(J) = DEV(I)
11
    CONTINUE
    CONTINUE
12
    N=N-1
    IF (N.LT.KKK) GO TO 3
    GO TO 8
    X(I)=0.
    Y(I) = 0.
    DEV(I)=0.
    R(I)=0.
    TITLE(I)=0.
    GO TO 3
93
    CONTINUE
    STOP
    END
```

- C. Steps in the Collection and Treatment of Saturation Current Data
- 1. Determine pressure and voltage ranges to be studied 2. Conduct i vs V experiments at each pressure 3. Tabulate averaged currents at each voltage Compute  $I_{iv}$  (intercept) and  $S_{iv}$  (slope) of saturation current plot 4. Tabulate  $I_{iV}$  and  $S_{iV}$  with respect to pressure 5. Compute N<sub>2</sub> drift 6. Correct N<sub>2</sub>  $I_{iV}$  and Sample  $I_{iV}$  for N<sub>2</sub> drift 7. Compute Sample drift correction 8. Correct Sample  $I_{iV}$  for Sample drift 9. Tabulate corrected  $I_{iV}$  with respect to pressure and time elapsed 10. Compute  $I_{ref}$  (N<sub>2</sub>) at 6.73 X 10<sup>20</sup> electrons cc<sup>-1</sup> 11. Compute Ratio of  $I_{iV}$  (sample)  $/I_{ref}$  (N<sub>2</sub>) = (normalized saturation 12. current) 13. Compute electron densities for sample temperature and pressures used 14. Tabulate  $R_{II}$  with respect to electron density Plot  $R_{TT}$  vs electron density 15.

D. Rate of Change of Activity of Ni-63 Beta-Source.

Fraction of change per unit time =  $\frac{C_0 - C_t}{C_0} = 1 - \frac{C_t}{C_0}$   $C_t = Activity at any time (after interval t)$   $C_0 = Activity @ t = 0.$   $\frac{C_t}{C_0} = e^{-(\frac{\ln 2}{t_{1/2}})t}$  In 2 = .69315  $t_{1/2}(Ni-63) = 125$  yrs. = 1500 mo.  $\frac{C_t}{C_0} = e^{-(\frac{.693}{.1500 \times 10^4 \text{ mo.}})X1 \text{ mo.}} = e^{-.000462}$ Note:  $e^{-X} = 1-X$  for x<<1  $1 - \frac{C_t}{C_0} = .000462$ ; Change of Activity per month = .0462% = 462 ppm.

Change per day  $\approx \frac{1}{30} \times 462 \text{ ppm} = 15 \text{ ppm}.$ 

- E. Fractional Energy Loss Due to Interception of  $\beta$  by Wires
- Looking at wire grid from ends of wires, the space available to any particle before it passes out of the region of the grid is a semicylinder whose cross section is π D, where D is the distance travelled before interception.



The fraction of that cross section which might intercept the  $\beta^{-}$  particle is at most  $\frac{W}{\pi D}$ 

2) Looking at the plane of the grid from above, the area of possible paths for any  $\beta^{-}$  particle is limited by the bulk of its home wire to  $\pi$  radians.



3) Of the total volume available to any  $\beta$  particle within a radius  $D_{max}$ , (the point farthest from it on any adjacent wire), the fraction which is available to intercept the particle is

P<sub>i</sub> = 
$$\frac{\int_{\theta=0}^{\theta=\theta_{max}} \frac{W}{\pi} d\theta}{\pi}$$
 where  $\theta_{max}$  corresponds to  $D_{max}$   
4)  
P<sub>i</sub> =  $\int_{0}^{\theta_{max}} \frac{W}{\pi^2} \frac{\cos \theta}{D_{min}} d\theta$  since  $D = \frac{D_{min}}{\cos \theta}$ 

5) Dimensions: Length of wire ≤ 1.75"; Length plated with Ni-63 = 1.00" Maximum length of any wire from a point directly across from a β<sup>-</sup> to the end of the wire is 1.375".

6) 
$$D_{min} = .101$$
" W = .010 ± .000] (Limit of Accuracy = 1%)  
for  $\overline{P}_i$ 

$$\frac{W}{\pi^2 D_{\min}} = \frac{.010}{(9.8697)(.101)} = .01003$$

7) 
$$P_i = \frac{W}{\pi^2} [\sin \theta]_0^{\theta} \max$$

8) Maximum: Tan 
$$\theta_{max} = \frac{1.375}{.101} = 13.61$$
 Minimum: Tan  $\theta_{max} = \frac{.375}{.101} = 3.713$   
Sin  $\theta_{max} = .9973$  Sin  $\theta_{max} = .9656$   
P<sub>i</sub> = .01000 P<sub>i</sub> = .00968

9) Center: Tan  $\theta_{max} = \frac{.875}{.101} = 8.663$ Sin  $\theta_{max} = .9934$ P<sub>i</sub> = .00996 Total P<sub>i</sub> = .01992

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10) If the probability distribution is linear, then  $P_i = k \cdot 1$ , where 1 is the distance from the center of the wire to the end of the Ni-63-plated length and  $k = \frac{P_{max} - P_{min}}{1}$ 

11) 
$$k = \frac{.00024}{.5} = .00048$$
  
12) Any P<sub>1</sub>: .01968 + k·1  
13) Mean:  $\overline{P}_1 = .01968 + \frac{\int_0^{0.5} P(1) 1 d1}{\int_0^{0.5} 1 d1}$   
 $= .01968 + k (.3333)$   
 $= .01968 + (.00048)(.3333)$   
 $= .01068 + .00016$   
 $\overline{P}_1 = .01984 \pm .00020$   
 $\overline{P}_1 = 1.984\%$  at vacuum  
 $= 1.98 \pm .02\%$   
 $= The fraction of  $\beta^-$  current lost to the wires at vacuum$ 

#### F. Collection Efficiency of Ionization Chamber

**Collection Efficiency = f = fraction of true ionization current which is actually measured.** 

References:

- Boag, J.W., "Ionization Chamber", in <u>Radiation Dosimetry</u>, G.J.
   Hine and G.L. Brownell, eds., Academic Press, Inc., 1956.
- (2) Thomson, J.J., and Thomson G.P., <u>Conduction of Electricity</u> <u>Through Gases</u>. VI. <u>General Properties of Ions and Ionization by</u> Heat and Light. Cambridge University Press, 1928.
- (3) McDaniel, E.W., <u>Collisional Phenomena in Ionized Gases</u>, John Wiley and Sons, Inc., 1964.
- (4) Moelwyn-Hughes, E.A., <u>Physical Chemistry</u>, Second Revised Edition, Pergamon Press, 1961.
- (5) Weidner, R.T. and Sells, R.L., <u>Elementary Modern Physics</u>, Allyn and Bacon, Inc., 1960.
- R = Total recombination through chamber space per unit of plate area per second
- q = Ionization Intensity ( $\mu$ A/cm
- d = Spacing between plates (cm)
- V = Potential between plates
- α = Recombination coefficient

e = Charge of one electron

 $k_1$  and  $k_2$  = Ion mobilities of the positive and negative ions

Reference f = l - fraction of ions recombining (1) p.153  $R = d(\alpha/e)(f^2q^2d^4)/6k_1k_2V^2$  $f = 1 - f^2(\alpha/e)(qd^4)/6k_1k_2V^2$ For spherical chambers,  $d = K_{sph}(a-b)$ b = radius of center electrode  $K_{sph} = [1/3(a/b + 1 + b/a)]^{1/2}$ 

For all chambers:

**Collection Efficiency:** 

f = 1 - R/qd

a = chamber radius

$$q = i/fd$$
  
 $i = current density (uA/cm2)$  (2) p. 166

Mobilities of Ions

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$$k_{1} = 35.9/(\alpha_{0}M_{r,1})^{1/2}$$
(3) p. 446  

$$\alpha_{0} = \text{Polarizability of the gas}$$
(units:  $a_{0}^{3}/\text{molecule}; a_{0} = 1\text{st Bohr Radius} = .528 \times 10^{-8} \text{cm})$   

$$M_{r,1} = \text{Reduced Mass of the Ion-Molecule System}$$
For  $N_{2}^{+}$  and  $e^{-}$  in  $N_{2}$   

$$\alpha_{0}(N_{2}) = 1.734 \times 10^{24} \text{ cm}^{3}/\text{molecule}$$
(4) p.383  

$$= 1.734 \times 10^{24} \text{ cm}^{3}/\text{molecule} \times (a_{0}/.528 \times 10^{-8} \text{cm})^{3}$$

$$= 1.734/.1472(a_{0}^{3}/\text{molecule})$$

$$\alpha_{0}(N_{2}) = 11.78 a_{0}^{3}/\text{molecule}$$

Reference

Reduce masses:

$$N_{2}^{+}, N_{2} \text{ system: } M_{r} (N_{2}^{+}, N_{2}) = \frac{(28.0129)(28.0134)}{56.0263} = 14.007$$
e<sup>-</sup>, N<sub>2</sub> system:  $M_{r} (e^{-}, N_{2}) = \frac{(5.488 \times 10^{-4})(28.0134)}{(.00054) + (28.0134)} = .0005488$ 

$$k_{e^{-}} = 35.9/[(11.78)(.0005488)]^{1/2} = 35.9/[.00645]^{1/2} = 35.9/.08041 = 446.5$$

$$k_{N_{2}}^{+} = 35.9/[(11.78)(14.0077)]^{1/2} = 35.9/[165.0]^{1/2} = \frac{35.9}{12.85} = 2.793$$

Equivalent plate spacing:

Let 
$$d = K_{sph}(a-b)$$
.  
 $K_{sph} = [1/3(a/b + 1 + b/a)]^{1/2}$  where  $a = chamber radius = 6.204$  cm  
and  $b = electrode radius = 2.540$  cm(1")

a-b = 3.665 cm a/b = 2.443 cm; b/a = .4094 cm;  $K_{sph}(a-b) = 4.151$  cm = d;  $d^4 = 297.0$ Ionization Intensity:  $q = \frac{i}{f \cdot d}$  (1) p. 166  $i = current density, \mu A/cm^2$ 

(Use i @ maximum field strength, to underestimate f)

Assume N<sub>2</sub> at pressures from 1 to 2 atm, Field from 1.0 to 2.0 kV Area of Ni-63 plating =  $(1 \text{ in})^2$  =  $(2.54 \text{ cm})^2$  = 6.45 cm<sup>2</sup>

$$i = \frac{1.95 \text{ nA}}{6.45 \text{ cm}^2} = 302\mu\text{A/cm}^2; \text{ f} \approx 1.00; \text{ d} = 4.151 \text{ cm}$$
$$q = \frac{302\mu\text{A/cm}^2}{(1.00)(4.151 \text{ cm})} = 72.8 \ \mu\text{A/cm}^3$$

(A more reasonable estimate may be 1/2 this amount for  $N_2$ )

Reference

Recombination Coefficient:

(2) p.36

Assuming recombination in N<sub>2</sub> is similar to that in Air and CO<sub>2</sub>, estimate  $\frac{\alpha}{e}$  to be 3500 ± 200 @ 800 torr and 8750 ± 500 @ 2000 torr to 14000 ± 800 @ 3200 torr

Positive root of the quadratic equation:  $(0 \le f \le 1)$ 

$$f = \frac{-1 + [1 + 4((\alpha/e)qd^{+})/(6k_1k_2V^{2})]^{1/2}}{2[(\alpha/e)qd^{4}/6k_1k_2V^{2}]}$$

Collection efficiency for  $\mathrm{N}_{\mathrm{2}}$  in our approximately spherical chamber

	_			_	_										
$k_{N2}^{+} = 2.793$				$\alpha_0(N_2) = 11.78 a_0^3/mo1.$						a = 6.204 cm					
$k_{e^{-}} = 446.5$			6	$6k_1k_2 = 7482$						b = 2.54 cm					
	800 torr					1600 torr				2400 ta	3200 tor	'n			
3000V:	99.9%					99.8%				99.7%	99.6%				
2000V:	99.7%				9	99.5%				99.3%		99.0%			
1000V:	99.0%					98.1%				97.2%	96.3%				
Summary:	0	800	torr,	f	is	reduced	by	0.9%	in	going	from	3000-	1000V.		
	0	1600	torr,	f	is	reduced	by	1.7%	in	going	from	3000-	1000V.		
	0	2400	torr,	f	is	reduced	Ьy	2.5%	in	going	from	3000-	1000V.		
	0	3200	torr,	f	is	reduced	bу	3.3%	in	going	from	3000-	1000V.		