

Conductivity Pulses Induced in Insulating Liquids by Ionizing Radiations

NORMAN DAVIDSON AND A. E. LARSH, JR.

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California*

(Received November 8, 1949)

Conductivity pulses due to electron collection have been observed in liquid and solid argon exposed to α - or γ -radiation. The maximum pulse sizes, P_M , for α -particles depend only on the field strength, E , and not on the electrode spacing, proving that the pulse limiting effect is columnar recombination and not electron trapping by impurities. The maximum pulse sizes obey the equation $(P_M/P_0) = 1 - \exp(-AE^3)$, where P_0 is the α -pulse size in an argon gas counter. The counting efficiency for α -particles is close to 100 percent, but there is some variation in pulse size due to variation of columnar recombination with angle of emission. No α - or γ -pulses were observed in liquid nitrogen or heptane, but weak α -induced pulses were observed in liquid methane.

The effects of nitrogen and oxygen in solution in liquid argon in decreasing the pulse sizes are interpreted as being due to electron capture by these molecules.

I. INTRODUCTION

THERE has recently been considerable interest in the study of crystal counters.^{1,2} In this experiment bound electrons in a crystal are excited into a conducting state by the passage of an ionizing radiation, and the rapid motions of these electrons through the crystal toward a collecting electrode are observed. If the freed electrons are trapped at sites in the crystal before they move a sufficiently large fraction of the distance to the collecting electrode, no voltage pulse is detected. From an elementary theoretical point of view one would expect that free electrons introduced into a pure liquid composed of molecules with no electron affinity would move in an applied field without being trapped. The study of liquid counters might therefore provide information about the electron trapping properties of various molecules. A practical difficulty with crystal counters is the development of space charge during operation due to the accumulation of non-mobile positive and negative charges at sites in the crystal. A successful liquid counter would avoid this

difficulty, because of the slow mobilities ($\sim 10^{-3}$ cm²/volt-sec.) of ions in liquids. For these reasons we have carried on the investigations on liquid counters described below. A brief account of our early results has already appeared,³ and G. W. Hutchinson⁴ has independently worked in the same field, A. N. Gerritsen⁵ has measured the d.c. ionization currents due to α -particles for liquid nitrogen, hydrogen, helium, and argon.

II. EXPERIMENTAL

a. Materials

"Welding Argon" supplied by the Linde Air Products Company was used without further purification. It was stated by the supplier to be better than 99.8 percent pure, with nitrogen the principal impurity, and with the oxygen content "nil." Further purification of the argon by passage through the deoxidizer described did not noticeably affect its counting characteristics.

Linde "High Purity Dry" nitrogen which is stated to be 99.99 percent pure was passed over reduced copper supported on diatomaceous earth at *ca.* 300°C, and over phosphorus pentoxide.⁶ Cylinder oxygen was passed over P₂O₅. Phillips Petroleum Company "Pure" methane, with a minimum purity of 99 percent, was used directly. The Phillips' "Pure" *n*-heptane of a stated minimum purity of 99 percent was washed with concentrated sulfuric acid and water, dried over potassium hydroxide, refluxed in vacuum over molten sodium, and then distilled into the liquid counter. The various gases were condensed into the counter tube using liquid air whose temperature was controlled when necessary by bubbling oxygen through it or by cooling it by evacuation.

b. Measurements

Figure 1 shows the ion chamber used for most of the measurements. A RaD-polonium source on a platinum

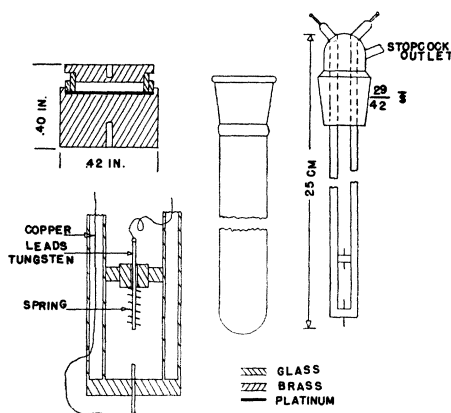


FIG. 1. Liquid ionization chamber.

* Contribution No. 1349.

¹ P. J. Van Heerden, *The Crystal Counter* (N. V. Noord-Hollandsche Uitgevers Maatschappij, Amsterdam, 1945).

² For a general summary, see R. Hofstadter, *Nucleonics* 4, No. 4, 2 (1949); 4, No. 5, 29 (1949).

³ N. Davidson and A. E. Larsh, Jr., *Phys. Rev.* 74, 220 (1948).

⁴ G. W. Hutchinson, *Nature* 162, 610 (1948).

⁵ A. N. Gerritsen, *Physica* 14, 381 (1948).

⁶ Pollock, Pringsheim, and Terwood, *J. Chem. Phys.* 12, 295 (1944); F. B. Meyer and G. Ronge, *Zeits. f. angew. Chemie* 52, 63 (1939).

foil could be held in place on the surface of the lower electrode by the glass spacers. Several glass spacers were used to give collecting electrode spacings (at the temperature of liquid air) of 0.094, 0.360, and 1.08 mm. Voltage pulses due to electron collection were amplified with a fast linear amplifier constructed according to the directions of Bell and Jordan.⁷ This instrument contains a pulse height selector for determining the size distribution of the output pulses. As used for most of our measurements, there was an instrumental rise time of about 4 μ sec. and a decay time of about 20 μ sec. The gain calibration was made using a well-shielded voltage divider and the trigger pulses from a P4-E M.I.T. Radiation Laboratory synchroscope. The capacitances of the counters and associated input circuit were measured with a General Radio Company Impedance Bridge, Type 650-A, at 1000 cycles/sec. These capacitances were: (1) Liquid counter, 0.094-mm spacing, containing liquid argon, plus input circuit, 30 μ mf; (2) the same, 0.4- or 1.1-mm spacing, 27 μ mf; (3) gas counter plus input circuit, 29 μ mf; (4) input circuit alone, 16 μ mf. That the capacitance measurements and the amplifier gain measurements were at least roughly consistent was shown by the observed maximum size of the polonium alpha-pulses of 1.015 mv in the argon gas counter. Using the value of 25.4 ev/ion pair for argon,⁸ the calculated pulse size for a 5.30-Mev α -particle is 1.15 mv. The visually estimated rise time of the pulses in the gas counter was 7.5 μ sec., the fall time, 20 μ sec.; this introduces a "clipping" correction of 83 percent, so the theoretical pulse size is 0.95 mv.

The counter tubes and preamplifier were housed in a 1½ ft. × 2 ft. × 2½ ft. grounded box shielded with copper screening and 0.020-in. sheet steel. With the preamplifier in the middle of this space and grounded to the box by a wire, there was considerable pick-up by the counter leads of the miscellaneous electrical disturbances in the laboratory. This was true even though multiple ground connections were avoided. The most effective measure in removing these difficulties was simply to mount the preamplifier chassis flush against the conducting walls of the box. It was also helpful to use batteries for a high voltage supply instead of a transformer-rectifier voltage source. The batteries were external to the box to avoid pick-up of radiated battery noise, and the voltage led into the counter through RC filters.

III. RESULTS AND DISCUSSION

a. Liquid Argon

Conductivity pulses due to α -particles and γ -rays have been observed with liquid argon. Large α -particle

⁷ W. Jordan and P. Bell, *Rev. Sci. Inst.* **18**, 703 (1947); Manhattan District Report, Mon. P-323, "Instructions for use of A-1 amplifier and preamplifier" (July 28, 1947).

⁸ Rutherford, Chadwick, and Ellis, *Radiations from Radioactive Substances* (Cambridge University Press, London, 1930), p. 81.

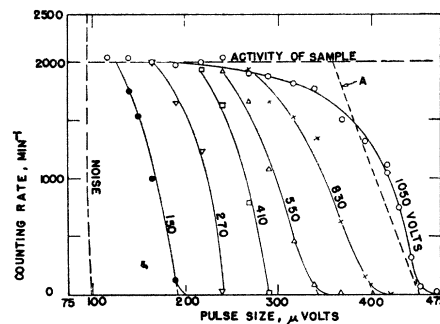


Fig. 2. Pulse size distribution curves for different collecting voltages (0.094-mm gap). (For all the curves except that at 1050 collecting volts, 10-sec. counts; one-minute counts for this case.)

pulses were observed only with the collecting electrode positive and hence are due to electron collection. Figure 2 displays a set of pulse height distribution curves for the 0.094-mm spacing. The maximum pulse sizes were determined by the indicated extrapolations, and by subtracting 95 μ volts for the contribution of noise. Figure 3 exhibits the dependence of the maximum pulse size, P_M (normalized to an input capacitance of 30 μ mf), on the field strength, E , for the three different electrode spacings. The plot is actually one of $\ln(1 - P_M/P_0)$ vs. $E^{\frac{1}{2}}$, where P_0 is the maximum calculated pulse size assuming that, just as in argon gas, an energy of 25.4 ev is required per electron and that every electron liberated moves all the way to the collecting electrode. The observed P_M 's are all less than one-half of P_0 . There is no evidence in Fig. 3 that the maximum pulse size has reached a saturation value at the voltages used, and hence no indication whether the energy per ion pair is different in liquid argon than in the gas. *The data of Fig. 3 show that the pulse size is dependent on the field strength alone and is independent of electrode spacing. Therefore the pulse limiting event for α -particles in liquid argon is recombination of the liberated electrons with the column of positive ions left in the track of the α -particle (columnar recombination) and not electron trapping.* The trapping hypothesis predicts that the pulse size would be inversely proportional to the electrode spacing for a fixed field strength. Indeed, the pulse sizes for the two larger spacings are slightly greater than those for the 0.094-mm spacing at the same field; we are unable to explain this small discrepancy. Hutchinson⁴ has already suggested that columnar recombination might be the cause of our relatively small pulse sizes.

We now consider the question of the causes of the distribution of pulse sizes for a given collecting voltage. We will discuss in detail the pulse size distribution curve for 1050 collecting volts and the 0.094-mm electrode gap displayed in Fig. 2. There is a plateau in the curve of counting rate vs. pulse size which corresponds closely to the counting rate of the sample observed in a gas counter (the horizontal line of Fig. 2). There is an observed spread in pulse size of about 250 μ volts. This

could be due to (a) variation in the contributions of noise to different pulses, (b) variation in pulse size with the angle of emission of the α -particles. Item (a) contributes only about 30 μ volts to the pulse size spread. This was determined by observations on pulses of uniform size from a pulse generator. Item (b) includes two factors. There is the possibility that the efficiency of columnar recombination varies with the angle of emission. There is also a geometrical effect since electrons liberated from an α -track that is perpendicular to the electrodes move on the average a smaller fraction of the electrode spacing to reach the collecting electrode than do electrons liberated from an α -track that is parallel to the collecting electrode and necessarily the maximum distance away from the collecting electrode. The calculated range of polonium α -particles in liquid argon is 0.05 mm, therefore assuming no difference in columnar recombination, pulses due to electron collection from α -tracks perpendicular to the electrodes should be of the order of 75 percent of the size of those due to α -particles moving parallel to the plates for the 0.094-mm spacing. (We do not consider in this approximate treatment the effect of the variation of specific ionization along a track in view of the difficulty in treating the dependence of the columnar recombination on this variable.) If θ = the azimuthal angle of emission of the α -particles, then the fractional number of α -particles between zero and θ is $1 - \cos\theta$. For the particular dimensions under consideration, the pulse size at angle θ is calculated to be $P_M(1 - (\cos\theta)/4)$ and the pulse size distribution curve is predicted to be $N(P) = 4(1 - P/P_M)$, where $(3P_M/4) < P < P_M$ and $N(P)$ is the fractional number of pulses of size greater than P . This is the dotted curve *A* of Fig. 2. (It must be remembered that the true pulse sizes, P , are obtained from those in Fig. 2 by subtracting 95 μ volts for the noise level.)

The reality of this geometrical effect as an influence on pulse size is most convincingly demonstrated by

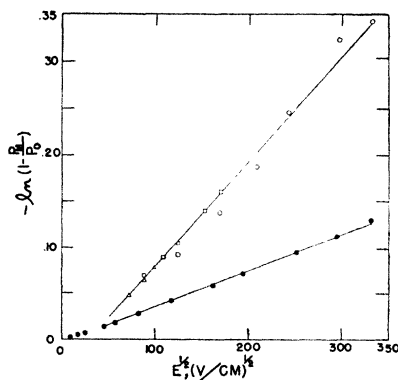


FIG. 3. Dependence of maximum pulse size, P_M , on field strength, E , for three different electrode spacings. (The pulse sizes have been normalized to an input capacitance of 30 μ mf.) \circ , \square , \triangle , 0.094, 0.36, 1.08-mm spacings; \bullet , Gerritsen's data (see reference 5) for the variation of the d.c. ionization current, I , induced in liquid argon by polonium α -particles, plotted in the form $\ln(1 - I/I_0)$ vs. E^2 .

TABLE I. Pulses in liquid argon with α -active electrode positive.*

Counting rate (percent of total)	Maximum azimuthal angle	Minimum pulse size (μ volts)	
		(obs.)	(calc.)
3	14°	70	84
17	34°	58	72
30	46°	46	61
75	76°	33	22

* 0.094-mm spacing, 1040 collecting volts.

observing the small pulses due to the collection of electrons at the lower (active) electrode when it is positive. Table I records some observations on this effect. (Calculation shows that for the narrow spacing used, the effects of Table I cannot be due to Ra-E β -rays.)

In the table, the azimuthal angles were calculated from the fractional counting rate for a given pulse size and the calculated minimum pulse sizes as $(P_M \cos\theta)/4$ (P_M being the maximum pulse size for the active electrode negative).

In view of the small pulse sizes involved, the agreement between calculations and observations in Table I is satisfactory. This in turn gives one confidence in the reliability of curve *A* of Fig. 2 to represent the variation of pulse size with angle of emission due to the geometrical factor. The discrepancy between the experimental curve and *A* may then be due to an increasing efficiency of columnar recombination for α -tracks with small θ . For example, at 1800 c/m (corresponding to an angle of emission of 26°) the pulse size is ca. 18 percent smaller than that (275 μ volts) predicted by curve *A*. There are so few α -rays that are closely parallel to the field (10°) that one has no information on the columnar recombination in this case.

To consider the variation of maximum pulse size with voltage one might look for a saturation curve of the type $P_M/P_0 = 1 - \exp(-AE^n)$. The plot of Fig. 3 shows that $n = \frac{1}{2}$ fits the data reasonably well; in view of the experimental uncertainties and the uncertainty as to real value of P_0 for liquid argon, we have not attempted to find a function that fits the data better. We can offer no theoretical explanation for the value $n = \frac{1}{2}$.

Gerritsen⁵ has observed the d.c. ionization current, I , induced in liquid argon by polonium- α 's that is plotted in Fig. 3 as $\ln(1 - I/I_0)$ where I_0 is the saturation current in argon gas. He finds much larger ionization currents in liquid argon and helium than in nitrogen or hydrogen. Furthermore, the dependence of current on field strength in nitrogen and hydrogen is in accordance with that expected on the basis of the theory of columnar recombination of heavy ions, and this is not the case for argon and helium. This is in accordance with our observations presented below that electrons can move freely through liquid argon but are trapped by nitrogen molecules. In Fig. 3 it is seen that Gerritsen's data also give a linear plot of $\ln(1 - I/I_0)$ vs. E^2 . The slope of this curve is about 0.4 of the slope of the

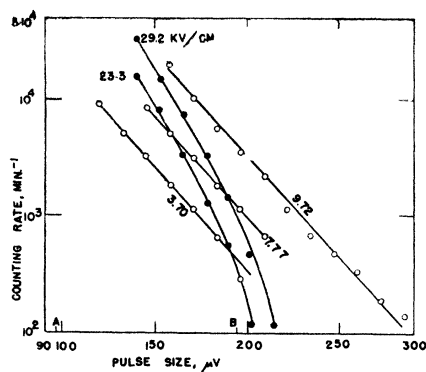


FIG. 4. Gamma-ray counting with liquid argon (the pulse sizes have been corrected for noise level). (A and B, maximum α -pulse sizes for 9.6 and 28.9 kv/cm, respectively.) ●, 0.36-mm gap; ○, 1.08-mm gap.

curve for our data on P_M/P_0 . Gerritsen's data for the average current should really be compared not with our values of P_M but with suitably averaged values of P obtained from the distribution curves of Fig. 2. This averaging process would recognize that there is no reduction in d.c. current in Gerritsen's measurements corresponding to the reduction in pulse size in our electron collection experiments due to the geometrical effect for which curve A of Fig. 2 was calculated. Without making detailed calculations, it is evident that the averaged value of P is not less than $0.9 P_M$ and that there is a real discrepancy between our results and those of Gerritsen. Small concentrations of electron trapping impurities in Gerritsen's argon that did not influence the columnar recombination but subsequently captured the electrons would not affect a d.c. ionization current. In view of our indications reported in a subsequent section that small concentrations of nitrogen in the argon reduce the pulse size by increasing the columnar recombination as well as by trapping electrons, it is conceivable that Gerritsen's low results are due to nitrogen impurity in the argon he used.

In concluding the section on α -particles in liquid argon we note that with the crude apparatus used for the data of our preliminary report,³ we underestimated the field at which conductivity pulses of a given size are obtained. We have not extended the qualitative observations recorded there that when the argon was solidified in the counter, presumably in a polycrystalline condition, conductivity pulses were still observed. Hutchinson⁴ has confirmed and extended these observations. One is led to believe that the height of the conduction band in crystalline argon is such that electrons can readily enter or leave the crystal from or to the vapor phase.

Figure 4 displays some pulse size *vs.* activity curves for Compton electrons from γ -rays in liquid argon. The data were obtained with a 1.7-mc radium needle mounted in the plane of the counting electrodes and at a fixed distance of about 2 cm away. These data agree

in a general way with Hutchinson's description⁴ of his experiences counting γ -rays in liquid argon. Although radium- γ 's are less energetic than polonium- α 's, there is less columnar recombination and the maximum pulse sizes observed are larger for the γ -rays than for the α 's at the same field. Because of geometrical effects, more large pulses are observed with the wider electrode spacings; and, of course, the pulse sizes are independent of the direction of the applied field. We do not know the causes of the variations of pulse size with field strength at a fixed electrode spacing.

b. Solutions of Oxygen and Nitrogen in Liquid Argon

In order to learn something about the electron trapping properties of oxygen and nitrogen molecules, we have investigated conductivity pulses due to α -particles with dilute solutions of these components in liquid argon. We set: $u(c, E)$ =drift velocity of an electron toward a collecting electrode in a field E and in a solution of concentration c (mole fraction) of the dilute component, $k(c, E)$ =probability of capture in unit time, $n(c, E)$ =number of electrons escaping columnar recombination from an α -track in such a solution, $P_s(c, E)$ =maximum pulse size for the solution, $n_0(E)$ =number of electrons escaping columnar recombination in pure argon, $P_M(E)$ =maximum pulse size in pure argon, l =electrode spacing, $m=u/k$. The quantity m is readily shown to be the mean drift distance of electrons before capture. By a well-known derivation⁹ one obtains

$$(P_s/P_M) = (n/n_0)(m/l)[1 - \exp(-l/m)]. \quad (1)$$

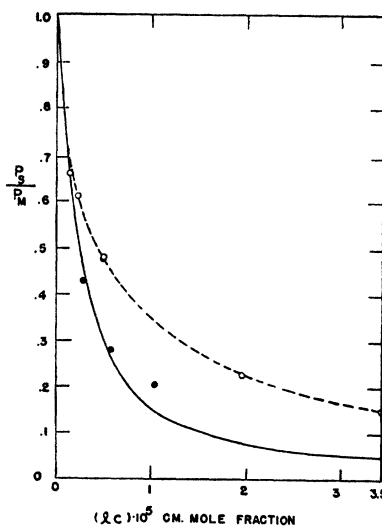


FIG. 5. P_s/P_M for solutions of oxygen in liquid argon as a function of lc . ○, 0.094-mm gap, 113 kv/cm; ●, 0.36-mm gap, 29 kv/cm. The dotted line goes through the experimental points for the narrow gap. The solid line is the theoretical curve of Eq. (1), assuming $(n/n_0)=1$ and $m=(1.55 \times 10^{-8}/c)$ cm.

⁹ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), p. 122.

The observed values of P_s/P_M for dilute solutions of oxygen in argon are plotted in Fig. 5 as a function of lc . The results plotted are for the maximum available field strengths for the two electrode spacings used because greater accuracy in the measurements was obtained in this way. However, with the 0.094-mm spacing, there was no marked dependence of P_s/P_M on E . Thus with $c = 2.6 \times 10^{-4}$, we observed for P_s/P_M 0.61 (113 kv/cm), 0.59 (87 kv/cm), 0.55 (58 kv/cm), 0.54 (29 kv/cm). The fact of electron trapping is unambiguously proved by the decrease in P_s/P_M with increasing electrode

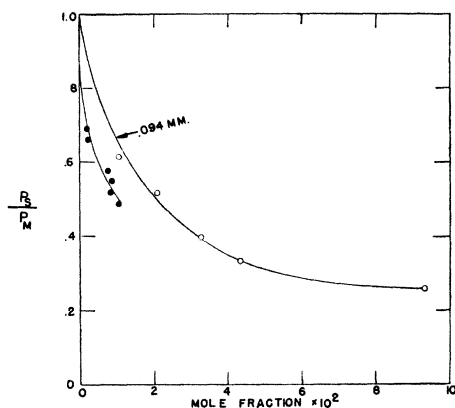


Fig. 6. Pulse sizes in solutions of nitrogen in argon, \circ , 0.094-mm gap, \bullet , 0.36-mm gap.

spacing (remembering that P_s/P_M is approximately independent of field strength). The plot of Fig. 5 shows that the variation of P_s/P_M with l fits Eq. (1) with the assumption that $n = n_0$ and indeed one cannot explain the variation of P_s/P_M with l unless n is approximately equal to n_0 at O_2 concentrations of about $1-2 \times 10^{-4}$ mole fraction.

For sufficiently dilute solutions one would expect that the mean drift path, m , would be inversely proportional to the concentration, c . However, with the short spacing and larger concentrations of O_2 the observed values of P_s/P_M are higher than those calculated from Eq. (1) at a fixed field strength assuming that $n = n_0$ and that $m = a/c$, using the more dilute solutions to determine a value of a , the constant. This deviation is also noticeable for the highest concentration ($c = 2.6 \times 10^{-4}$) used with the 0.37-mm gap. It seems improbable that $n/n_0 > 1$ for high concentrations of oxygen and we therefore propose that the equation $m = a/c$ does not hold at high concentrations ($> 3 \times 10^{-4}$). This is not unreasonable for the following reasons. The capture cross section by oxygen molecules is dependent on the agitation velocity of the electrons in the liquid and the mean agitation velocity probably decreases in the presence of small quantities of oxygen.¹⁰ Now, k , the probability of capture in unit time, equals the mean

agitation velocity times the capture cross section times the concentration of oxygen molecules in units of molecules per cc. We do not know how the capture cross section depends on the electron velocity. However the contribution of the first term is to make k decrease as the agitation velocity decreases. Since $m = u/k$, and u increases as the agitation velocity decreases,¹⁰ there are two known factors which would make m increase with decreasing agitation velocity.

Since the drift velocity is expected to be proportional to the field strength and k should not be strongly dependent on the field, it is surprising that P_s/P_M is approximately independent of the field strength. This probably means that the drift velocity is not proportional to the field strength, but a constant. The same situation occurs at high field strengths in argon gas.^{10,11} The value of E/p for argon gas at which the drift velocity becomes a constant is about 1 volt per cm per mm Hg. Using p simply as a measure of density, the values of " E/p " for liquid argon in our work are in the range of 0.015–0.15.

Assuming the order of magnitude figures for the drift velocity and the mean agitation velocity in liquid argon in a field of 10^4 – 10^5 volts/cm of 10^6 cm/sec. and 2×10^8 cm/sec. (this latter figure corresponding to a mean agitational energy of 10 eV¹⁰) one calculates from the values of m of ca. 0.016 cm for a concentration of O_2 , c of 10^{-4} (obtained from Fig. 5) a value of the cross section for electron capture by O_2 molecules of 10^{-19} cm²/molecule, using the relation stated above.

As shown in Fig. 6, the concentrations of N_2 required to diminish the pulse size a given amount are about 20 times greater than the equivalent O_2 concentrations. The approximation that the nitrogen is present as a very dilute solution and functions only as an electron trapping impurity without affecting n/n_0 or the velocity distribution of the electrons (and hence the capture cross section) does not work at all. Just as in the oxygen case, the values of P_s/P_M are independent of field strength. Thus with 1.04 percent N_2 , we observe $P_s/P_M = 0.61$ (111 kv/cm), 0.57 (86 kv/cm), 0.61 (56 kv/cm), 0.65 (43 kv/cm) and 0.67 (28 kv/cm). Similar results were obtained with 2.08 percent N_2 . The fact displayed in Fig. 6 that for a fixed N_2 concentration, the value of P_s/P_M decreases as the electrode spacing increases proves that electron trapping by N_2 molecules does take place. One can fit the data at $c = ca. 2.5 \times 10^{-3}$ by assuming that $m = 0.028$ – 0.12 cm and that $n/n_0 = 0.94 \pm 0.1$. To fit the data at $c = ca. 1$ percent one must assume that $m = 0.028$ – 0.12 cm and that $n/n_0 = 0.7 \pm 0.1$. Furthermore the values of P_s/P_M do not fall off as rapidly with N_2 concentration (for the short spacing) as would be expected if n/n_0 were constant and $m = a/c$. There are indications therefore that n/n_0 decreases with increasing concentration of nitrogen and

¹⁰ J. Allen and B. Rossi, "Time of collection of electrons in ionization chambers," MDDC 448, United States AEC, Oak Ridge, Tennessee (1944).

¹¹ D. E. Hudson, "Method of measuring the drift velocity of electrons in gases," MDDC 524, United States AEC, Oak Ridge, Tennessee (1946).

that m is not inversely proportional to the concentration. In view of the experimental inaccuracy, more precise conclusions are not possible.

c. Other Materials

With purified nitrogen no α -induced pulses were observed with the 0.094-mm spacing and no γ -induced pulses with the 1.0-mm spacing (the large spacing being more favorable for the detection of γ -pulses). The failure to obtain α -pulses might be attributed to a high efficiency for columnar recombination in liquid nitrogen but presumably with the relatively low specific ionization of the Compton electron ejected by a γ -ray the failure to observe γ -induced pulses is due to electron capture by nitrogen and confirms the conclusion of the preceding section that N_2 molecules do have an electron affinity.

We have observed no α -induced pulses with purified heptane, either at 0°C or -80°C, and Hutchinson⁴ observed no γ -induced pulses in purified hexane. However with methane just above its triple point we have observed weak α -induced pulses with 10^6 volts/cm and the 0.094-mm electrode spacing. The pulses were about 65 μ volts above noise. Because of the very weak pulses and the relatively low purity of the methane we have not tried to investigate this substance further to distinguish between the effects of columnar recombination and of electron trapping.

IV. ACKNOWLEDGMENT

Without the financial support of the ONR this work could not have been performed. We are indebted to Mr. Alvin Tollestrup for many helpful conversations about the operation of our amplifier and associated problems.

Do the Equations of Motion Determine the Quantum Mechanical Commutation Relations?

EUGENE P. WIGNER

Palmer Physical Laboratory, Princeton University, Princeton, New Jersey

(Received November 9, 1949)

The commutator of the Hamiltonian with the operator corresponding to any physical quantity gives the operator which corresponds to the time derivative of that quantity. One can ask, hence, whether the postulate, that the quantum mechanical operators obey the classical equations of motion, uniquely determines the commutation relations. The answer is found to depend on the form of the Hamiltonian and is in the negative for a free particle and for the harmonic oscillator.

1. SCHRÖDINGER¹ obtained his wave mechanical equation by postulating that the waves' motion correspond to the classical motion of a particle if the field of force in which it is moving does not change too rapidly with position. Later on, Ehrenfest² has shown that Schrödinger's work can be summarized most neatly by observing that the operators in the Heisenberg picture satisfy the classical differential equations:

$$\dot{q} = \partial H / \partial p; \quad \dot{p} = -\partial H / \partial q \quad (1)$$

if one assumes that the Hamiltonian has the simple form

$$H = p^2/2m + V(x). \quad (2)$$

As is well known, the time derivative of any operator in the Heisenberg picture is its commutator with the Hamiltonian so that (1) is equivalent with (2) and

$$(i/\hbar)[H, q] = \dot{q}; \quad (i/\hbar)[H, p] = \dot{p}, \quad (1a)$$

or

$$(i/\hbar)[\frac{1}{2}p^2, q] = \dot{q}; \quad (i/\hbar)[V, p] = \dot{p}. \quad (3)$$

These equations are usually derived from the Heisenberg-Born-Jordan relation

$$[p, q] = -i\hbar. \quad (4)$$

Since, however, (1) and (1a) have a more immediate physical significance than (4) (see in particular Ehrenfest's discussion), it is natural to ask whether, conversely, (4) can be derived from (1a). The present writer has considered this question some time ago but its significance in consequence of Heisenberg's recent paper³ and of their own work has been pointed out to him only recently by Pais and Uhlenbeck.

Some doubt on the fundamental nature of relations of the type (1a) must arise, of course, even apart from the results of the present analysis, by the observation that Dirac's equation of the electron does not lead to the classical equation of motion for the operators. Furthermore, because of the non-commuting character of the p and q , there are many forms in which the Hamiltonian can be written. In particular, in the example to be discussed below, $H = \frac{1}{2}(x + iv)(x - iv)$ could

¹ E. Schrödinger, *Abhandlungen zur Wellenmechanik* (J. A. Barth, Leipzig, 1927).

² P. Ehrenfest, *Zeits. f. Physik* 4, 455 (1927).

³ W. Heisenberg, *Zeits. f. Physik* 123, 93 (1944), p. 108 ff.