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# On the Role of Polyatomic Gases in Fast Counters

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The polyatomic gas serves a twofold purpose: (1) to quench ultraviolet photons and (2) to quench secondary emission by positive ions reaching the cathode. The characteristic property of a polyatomic molecule which is of importance for the operation of a fast counter is the large probability of predissociation from excited electronic states. The quenching of ultraviolet photons in the initial avalanche occurs through photo-decomposition of the polyatomic gas. In a fast counter containing a self-quenching mixture the polyatomic gas has invariably a lower ionization potential than the monatomic constituent. The positive ions make $10^5$ collisions in crossing the counter and the electron transfer probability ensures that the positive ion sheath, when it reaches the cathode, is composed entirely of polyatomic ions. These are neutralized at about $10^{-7}$ cm from the wall and the excited neutral molecules predissociate in $10^{-13}$ sec. before they can liberate a secondary electron by an inelastic collision with the wall. With no supply of secondary electrons the discharge terminates. Other features of fast counter behavior are discussed and some of the conclusions reached have been checked experimentally.

## INTRODUCTION

THE terms "fast" or "self-quenching" counter have been applied in recent years to that type of Geiger-Mueller counter in which the discharge terminates because of an internal process. These counters may be operated with comparatively low resistances and do not go into a continuous discharge except at high overvoltages. In order that a counter may operate as a fast counter, it must be filled with a certain minimum amount of polyatomic gas as a constituent. "Slow" or "non-self-quenching" counters, on the other hand, are filled with any monatomic or diatomic gas or mixture of such gases, and this type of counter goes into a continuous discharge unless operated with a high resistance or a vacuum-tube quenching circuit. Fast counters have been studied by Trost,[1] Ramsey,[2] Stever,[3] Korff,[4] and others. These investigations have dealt with the types of gas suitable for filling the counters, with measurements of the wire potential as a function of time, with measurements of dead time and recovery time, etc. A theory of the discharge mechanism in a slow counter has been given by Montgomery and Montgomery,[5] and their predictions are in good agreement with the observations of Ramsey, Trost, and others. The Montgomery theory has been extended to fast counters by Stever.[3] However, the role of the polyatomic gas in the discharge process has not as yet been explained. It will be shown here that the characteristic property of the polyatomic molecule which is important for the operation of a counter is the short lifetime of the excited electronic states against predissociation.

The excited electronic states of a diatomic molecule have sharp rotational levels well above the dissociation energy of the molecule, and predissociation is only an occasional phenomenon. In polyatomic molecules containing four or more atoms, predissociation is the rule rather than the exception, and the absorption spectrum in the ultraviolet shows diffuse absorption bands with the rotational structure obliterated, as well as regions of continuous absorption. This is essentially due to the opportunities for "crossing over" provided by the many intersections of the potential energy hypersurfaces extending over a wide range of energies. The heavier the molecule, the more diffuse is the spectrum and the more likely is predissociation. Light polyatomic molecules present an intermediate case, and the spectroscopy and photochemistry of each must be considered separately to determine the probable result of a given excitation.

It is to be noted that three distinct types of "quenching" are involved in the operation of a fast counter: (a) quenching of photons in the initial avalanche, (b) electrostatic quenching of the avalanche by the positive ion space charge,[5]

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[1] A. Trost, Zeits. f. Physik **105**, 399 (1937).
[2] W. E. Ramsey, Phys. Rev. **57**, 1022 (1940).
[3] H. G. Stever, Phys. Rev. **61**, 38 (1942).
[4] S. A. Korff, Rev. Mod. Phys. **14**, 1 (1942).
[5] C. G. Montgomery and D. D. Montgomery, Phys. Rev. **57**, 1030 (1940).

and (c) quenching of the secondary emission when the positive ions reach the cathode. The quenching of the discharge involves both the electrostatic quenching and the quenching of secondary emission. We propose to discuss the role of the polyatomic gas in quenching cases (a) and (c).

## PHOTON QUENCHING

First let us examine the role of the polyatomic gas in the initial avalanche. Common polyatomic constituents of counters are methane and alcohol vapor. Let us consider an argon-methane counter operating in the "proportional" region, in which the size of the pulse is proportional to the number of ions formed in the initial ionizing event. A theory of the formation of the avalanche in this case has been given by Rose and Korff.[6] Assuming that the electrons multiply by collision and that photoelectrons do not contribute to the cascade, they obtain a formula for the amplification or multiplication factor which agrees well with experiment as long as a sufficient amount of methane is present in the counter. When the relative or absolute amount of methane is reduced too far, the amplification factor is found to rise more steeply with increasing voltage than predicted by the formal, thus indicating an additional source of electrons. The dependence of this effect on the nature of the cathode surface led Rose and Korff to suggest that photoelectrons from the cathode were contributing to the avalanche. When the counter voltage was raised sufficiently, all the curves deviated from the formula. Rose and Korff point out that the inelastic collisions of electrons with methane molecules, leading to rotational and vibrational excitation, will dissipate the energy of the electrons and thus reduce the number of ultraviolet photons emitted in the avalanche. This cannot be the most important factor, however, in the quenching of the photons by the polyatomic gas since the greatest multiplication takes place in the high field region near the wire where the electrons gain enough energy in one free path to excite or ionize the argon atoms. Furthermore, a diatomic molecule should serve similarly, though less effectively, in dissipating the energy, and no amount of diatomic gas will quench the photon production. Rose and Korff have also suggested that collisions which cause electronic excitation of the polyatomic molecule will usually result in decomposition rather than in photon emission. This is in agreement with other evidence to be discussed below, and is supported by experiments of Glockler[7] in which electrons with 17-ev energy introduced into a methane-filled photo-cell produced no measurable photoelectric current. We wish to emphasize here that in a counter containing a mixture of gases the principal role of the polyatomic gas in the avalanche is to absorb the ultraviolet photons emitted by the inert gas (argon). Many photons originate in the avalanche from excited argon atoms. Ranging in energy from 11.5 to 15.7 ev, these photons would liberate electrons from the cathode (photoelectric threshold about 4 ev), were they not absorbed in the gas. Since a gas mixture containing fifty percent argon to fifty percent ether shows no evidence of cathode effect, according to Rose and Korff, it is evident that the argon photons are absorbed by ether molecules before they reach the cathode. This is also in accord with Ramsey's[8] double-counter experiment in which it was shown that when counter *A* discharged, if the photons from this discharge could reach the interior of counter *B*, then counter *B* discharged every time when the two were filled with a non-quenching gas (argon), and only at random times when the two were filled with a quenching gas (alcohol).

We inquire next into the details of the absorption act. When a molecule absorbs an ultraviolet photon and passes into an excited electronic state, there are several possible competitive modes of de-excitation: (1) decomposition (dissociation or predissociation), (2) radiation (fluorescence), and (3) deactivation by collision. Process (3) cannot occur in less than $10^{-8}$ sec., which is the collision time in an ordinary counter. Process (2) involves a radiation lifetime of $10^{-8}$ sec. Process (1), when possible, occurs within $10^{-11}$ to $10^{-13}$ sec. depending on the breadth of the levels. If the rotational structure is obliterated, the lifetime is about 100 times longer than if the vibrational structure is obliterated (continuous absorption). Diatomic molecules, in

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[6] M. E. Rose and S. A. Korff, Phys. Rev. **59**, 850 (1941).

[7] G. Glockler, Proc. Nat. Acad. Sci. **11**, 74 (1925).

[8] W. E. Ramsey, Phys. Rev. **61**, 96 (1942).

general, as well as certain light polyatomic molecules possess stable electronic states with well-defined vibrational-rotational structure well above the dissociation limit or limits of the molecule. Excitation of the molecule into this region of energy results in re-emission of the absorbed photon or fluorescence and only rarely in dissociation. Hence, the photons produced in the discharge would not be quenched by a diatomic gas. On the other hand, if we examine the spectroscopic and photochemical data[9] for methane, ammonia, and other gases used in fast counters for which data are available, we can understand why these gases are photon-quenching. The photo-decomposition of methane in the ultraviolet is well known and the absorption spectrum, taken at a pressure of 1 mm of mercury, shows continuous absorption from 1450A down to at least 850A, the limit of observation. The ultraviolet photons emitted by excited argon atoms range from 1070A to 790A; hence, they are quenched by methane. Ammonia vapor also photodecomposes in the ultraviolet, and the spectrum shows continuous absorption below 1200A. Hence, ammonia also quenches the argon photons.

Evidence of the decomposition of the alcohol vapor in a fast counter has been obtained by Spatz;[10] the decomposition in the initial avalanche is to be attributed partly to electron impact and partly to photo-dissociation. As we shall see later, further decomposition occurs when the alcohol ions reach the cathode. The primary decomposition products are usually free radicals which combine to form a miscellaneous assortment of organic molecules. Some of these decomposition products will be quenching gases; however, with continued use of the counter all of the larger vapor molecules are broken up and the end products of the decomposition are a non-quenching gas, such as hydrogen or oxygen, and hydrocarbon goo deposited on the walls.[11] These considerations explain why fast counters go bad with continued use. Since about $10^{10}$ alcohol ions are decomposed at the cathode in each discharge, as will be explained in the next section, and since there are altogether about $10^{20}$ alcohol molecules in the counter, the counter will go bad after about $10^{10}$ counts. This is in accord with Spatz's observations. These considerations further explain why a methane counter has a shorter life than an alcohol counter. Methane is already far down the list of decomposition products of alcohol and itself can decompose only once or twice before it is reduced to a non-quenching mixture. We can also understand why argon must be mixed with a greater proportion of methane than of alcohol to produce a photon-quenched counter, i.e., a counter with no cathode effect. This is due partly to the greater number of vibration-rotation levels available for inelastic electron impacts in the case of the alcohol counter and partly to the higher quantum yield of the photo-decomposition of alcohol.

Some of the results of Wilkening and Kanne[12] on localization of the discharge will be examined next. The discharge in the Geiger region normally spreads the entire length of the wire in both slow and fast counters.[3] A reduction in the field near the central wire by some artificial means, or the presence of an obstacle such as an insulating bead, will interrupt the spread of the discharge in a fast counter but not in a slow counter. In the latter case, photoelectrons from the cathode spread the discharge beyond the obstacle. Wilkening and Kanne used various devices to interrupt the spread of the discharge and measured the effectiveness of the localizing devices in various gases. Fast counters showed 100 percent "localization." However, a mixture of 1 cm of methane with 9 cm of argon showed only a 50 percent localization. This is clearly due to the fact that the photon-quenching is incomplete in this case, as we may verify from the amplification factor curves given by Rose and Korff; at 10-cm pressure even a 50 percent argon-methane mixture shows evidence of appreciable photo-effect. Counters filled with monatomic and diatomic gases showed "zero localization," or complete spread of the discharge, corresponding to the total absence of photon-quenching. There should exist a close correlation between the

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[9] Cf. Rollefson and Burton, *Photochemistry* (Prentice-Hall, New York, 1939). Data on the absorption spectrum in the ultraviolet of many polyatomic molecules may be found in tables at the end of the review article by H. Sponer and E. Teller, Rev. Mod. Phys. **13**, 75 (1941).

[10] W. D. B. Spatz, Phys. Rev. **64**, 236 (1943).

[11] L. M. Yaddanapalli, J. Phys. Chem. **10**, 249 (1942).

[12] M. H. Wilkening and W. R. Kanne, Phys. Rev. **62**, 534 (1942).

extent of localization and the length of the proportional region. It is well known that fast counters have a much longer proportional region than slow counters at the same total pressure. This is due to the more rapid rise of the amplification factor of a slow counter with increasing voltage, which is in turn due to the photoelectric effect at the cathode. Thus, the spreading of the discharge beyond an obstacle and the rapid rise of the amplification factor are due to the same cause: photons in the avalanche. The counters found by Wilkening and Kanne to show 100 percent localization are all counters containing heavy polyatomic vapors which are present in sufficient amount to absorb out the argon photons. The methane-argon counter showing 50 percent localization has a short proportional region, as may be inferred from Fig. 2 of reference 6. Counters filled with diatomic gases go over directly into a continuous discharge without any observable proportional counting, and show zero localization.

Finally, we mention a further consequence of the photon-quenching, which has already been pointed out by Weisz[13] and which is of minor importance for most counters. In a slow counter, some of the photoelectrons produced at the cathode will attach themselves to neutral molecules to form negative ions which drift in toward the central wire. In the high field near the central wire the electron will detach itself and start another avalanche unless the potential across the counter is below the starting potential at this time. Since the probability of electron attachment is very small for most counter gases, this effect will be unimportant except in the case of oxygen, where one collision in $10^4$ leads to attachment. Since the photoelectrons make about $10^4$ collisions in traversing the counter, negative molecular ions $O_2^-$ will play a role in the discharge.

## SECONDARY EMISSION QUENCHING

We consider next the transition from the proportional region to the Geiger region in which the size of the pulse is independent of the number of ions formed in the initial ionizing event. At the threshold voltage of the Geiger region, the amplification factor theoretically rises to infinity; in practice the Geiger threshold corresponds to an amplification factor between $10^8$ and $10^{12}$. Let us assume that the counter has a negligible resistance in series with it. Then when the Geiger threshold is reached, a slow counter will go into a "continuous" discharge, whereas a fast counter will give a single sharp pulse. Because of the absence of resistance, the counter is at operating potential during the entire time that the positive ions are moving out to the cathode. The electric field intensity in the vicinity of the wire is below the threshold field until the ions have moved out to the "critical distance." [3] The positive ions then have drift velocities of the order of one-tenth their thermal velocities and the kinetic energy they acquire between collisions is less than 0.1 ev. Thus, they can neither excite nor ionize, so that if no further ionizing particles enter the counter, nothing happens until the ions reach the cathode and are neutralized. It is at this juncture that the behavior of an argon-filled counter differs from that of a methane-filled counter. Secondary emission takes place in the argon counter and, since the counter is at operating potential at this time, the entire cycle is repeated. Thus the discharge in a slow counter is self-perpetuating although the avalanches are intermittent. In a methane counter, on the other hand, the discharge is terminated when the methane ions are neutralized, and no secondary emission can occur. The explanation of this is to be found in the decomposition of the neutralized methane.

Details of the neutralization act and subsequent secondary emission will be considered next. When an argon ion approaches to within $10^{-7}$ cm of the cathode surface, the field of the ion becomes great enough to extract an electron from the metal. An electron near the top of the Fermi distribution may penetrate the barrier separating the potential well of the metal from the potential well of the ion. The neutralized atom is formed in an excited state, the energy of excitation being close to $I-\phi$, where $I$ is the ionization energy of the atom and $\phi$ the work function of the metal (in the case of argon ions and a copper cathode, the neutralized atoms are formed in the excited state at 11.5 ev). The critical distance of approach at which the probability of neutralization approaches unity,

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[13] P. Weisz, Phys. Rev. **62**, 477 (1942).

has been calculated by Oliphant and Moon,[14,15] using the Fowler-Nordheim formula. The probability of neutralization is an extremely sensitive function of the distance and for ions of thermal velocities approaching a copper surface the critical distance is about $5\times 10^{-8}$ cm. Thus, neutralization must take place before the ions are $5\times 10^{-8}$ cm from the wall, and the neutralized atoms should reach the wall in about $2\times 10^{-12}$ sec. Many atoms, however, do not reach the wall since the momentum communicated to the ion on neutralization is of the same order of magnitude as its initial thermal momentum. It has been found experimentally that $He^+$ ions which collide with an outgassed platinum surface at a glancing angle escape largely as neutral atoms in the metastable state. This indicates that an ion may be neutralized without making an inelastic collision with the wall. Many neutralized atoms, however, will approach the surface close enough to transfer their excitation energy to an electron in the metal, resulting in the emission of a secondary electron if $I>2\phi$. The probability of secondary emission by an excited atom approaching the surface has been calculated by Massey;[16] according to Massey's formula an atom of thermal velocity must approach to within $2\times 10^{-8}$ cm of the surface to make secondary emission probable, i.e., the wave functions of the atomic and metallic electrons must overlap. Since the radiation lifetime of the excited state of argon formed on neutralization is $10^{-7}$ sec., many of the argon atoms will liberate electrons from the cathode.

Let us now consider what happens when a methane ion captures an electron from the wall. The ionization energy of methane is 14.5 ev and the molecule resulting from the recombination has therefore the same excitation as a molecule that has absorbed light of wave-length 1200A. The spectrum of methane, as has been previously mentioned, shows continuous absorption below 1450A, indicating a lifetime against decomposition of the order of $10^{-13}$ sec. for the excited molecule. If this figure were exact and if the molecule required $2\times 10^{-12}$ sec. after neutralization to reach the wall, only about one molecule in $10^9$ could reach the wall before decomposing. We can suppose that the electrostatic image force orients the approaching polyatomic ion so that the charged end faces the surface; thus, neutralization occurs when the front end of the ion is $5\times 10^{-8}$ cm from the surface and about the same time is required to reach the surface as for the neutralized atom. Even after the polyatomic molecule comes into contact with the surface, i.e., within range of the van der Waals forces, a transfer of electronic excitation energy from the chemical bond in which it was originally localized, across several other bonds to an electron in the metal, is still less likely than a decomposition. The secondary emission is therefore very small. We must also note that a radiation lifetime of $10^{-7}$ sec. implies that one molecule per $10^6$ will radiate instead of decomposing. Since the photoelectric yield for the cathode surfaces used is of the order of $10^{-4}$ electrons per quantum, the secondary emission from this source amounts to one electron per $10^{10}$ incident positive ions. We take this figure to represent the total secondary emission.[17]

The average number of ions formed in a fast counter avalanche at the beginning of the Geiger region is about $10^9$. Hence, we can understand why the secondary emission is quenched and a single sharp pulse obtained from a counter filled with methane. In order to determine whether a given gas by itself will make a fast counter, we have to investigate its absorption spectrum at wave-lengths corresponding to an excitation energy of $I-\phi$. If the absorption spectrum is diffuse or continuous, corresponding to decomposition in this region, then the gas will make a fast counter. To take another example: The ionization energy of ethyl alcohol is 11.3 ev and the neutralized molecule is formed about 1700A above the ground state. The spectrum of the vapor shows continuous absorption below 2000A, and this is accompanied by photo-decomposition. The quantum yield of the photo-decomposition is of the order of unity. Hence, we should expect alcohol vapor to make a good fast counter. A diatomic molecule generally possesses discrete

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[14] M. L. E. Oliphant and P. B. Moon, Proc. Roy. Soc. **A127**, 388 (1930).

[15] M. L. E. Oliphant, Proc. Roy. Soc. **A124**, 228 (1929).

[16] H. S. W. Massey, Proc. Camb. Phil. Soc. **26**, 386 (1930).

[17] Recombination of secondary electrons with incoming positive ions will further reduce the chance of producing a new avalanche.

states between the dissociation energy and the ionization energy; thus, on neutralization a diatomic molecule will not decompose. This explains why counters filled with diatomic gases show slow counter action. Since a heavy organic molecule has a large probability of predissociating at all energies so that the ultraviolet absorption spectrum is everywhere diffuse or continuous, such a gas will invariably make a fast counter. The triatomic gases must be considered separately. The absorption spectra of $H_2O$, $CO_2$, $N_2O$, $SO_2$, $H_2S$, and $CS_2$ show bands with diffuse rotational structure converging on the ionization energy of the molecule as a limit. The broadening of the levels would correspond to a lifetime of the order of 100 times that of a heavy molecule, hence secondary emission would be much more probable. Some experiments we have performed with counters filled with the above-mentioned triatomic gases (connected to low resistances) gave no evidence of a Geiger region.

A further consequence of the mechanism of secondary emission quenching outlined above is that the frequency and multiplicity of multiple pulses should increase slowly along the plateau of a fast counter. The numerical estimates of secondary emission given above would lead one to expect about one double pulse in ten or one triple pulse in one hundred at the beginning of the Geiger region. This is roughly in agreement with what one observes on the oscilloscope screen. As the voltage across the counter is raised, the charge collected per count is found to vary linearly with the over-voltage and measurements along part of the plateau show that the charge increases by a factor of more than ten (see Appendix). An increase in the number of ions reaching the cathode results in an increased secondary emission and a corresponding increase in the frequency and multiplicity of multiple pulses. From the numerical estimates given above one would expect that toward the end of the plateau several secondary electrons on the average would be emitted when the positive ion sheath reached the cylinder. Under these circumstances practically every pulse would be a multiple of large multiplicity; in fact, the oscilloscope shows sprays of multiple pulses toward the end of the Geiger region. If electronic circuits of high resolving power for fast counting are used with the counter, these multiple pulses will give rise to many spurious counts. The slope of the counting-rate plateau is thus to be attributed to the increasing frequency and multiplicity of the multiple pulses leading to an increasing number of spurious counts; and the Geiger region terminates when the secondary emission becomes great enough to make the discharge self-sustaining. In order to make the plateau as flat and long as possible, the secondary emission must be small, and this implies that the polyatomic molecules used should have a short lifetime against dissociation and the photoelectric efficiency of the cathode material should be low. It has been found empirically that fast counter action is improved by a treatment of the cathode surface which reduces the photoelectric efficiency, e.g., the $NO_2$ treatment of copper.[3] It has been suggested that the factor which actually limits the width of the plateau is the occurrence of spurious counts due to "a sensitive condition of the surface of the cathode from which are emitted electrons when an electric field is present." [5] The fields at the cathode or even at the anode ($10^4$ v/cm) are not great enough to produce field emission for which a field of about $10^7$ v/cm is required. Unless the metallic surfaces are rough or the central wire has become pitted, this effect will be unimportant compared with the spurious counts arising from multiple pulses.

So far the discussion has been restricted to fast counters containing a pure polyatomic gas. If we consider next a self-quenching counter which contains a mixture of a quenching and a non-quenching gas, the question arises how the secondary emission is suppressed. Since a counter containing 90 percent argon to 10 percent alcohol is self-quenching, it is necessary to explain why no argon ions reach the cathode when there is a small amount of alcohol present. The explanation depends on the relative size of the ionization potentials of the two gases: 11.3 volts for $C_2H_5OH$ and 15.7 volts for argon. In the first place, the positive space charge formed in the initial avalanche must have a greater proportion of alchol ions than would be expected from the relative concentrations. This is partly due to the fact that the avalanche electrons can ionize alcohol molecules before they have acquired enough energy to ionize argon atoms, and the ionization cross sections are proportional to the excess energy of the electron above the ionization energy. Also, the ionization efficiency in $C_2H_5OH$ probably exceeds that in argon because of the greater number of electrons per molecule. However, the energies of the electrons are in all cases sufficient to produce a number of argon ions comparable to the number of alcohol ions. The reason why a negligible number of argon ions reaches the cathode is that electron transfer takes place during the passage of the ion sheath across the counter. During this time the argon ions make about $10^5$ collisions with alcohol molecules, and since the ionization energy of the argon atom is greater than the ionization energy of the alcohol molecule, an electron can be transferred from the molecule to the ion. The transfer of an electron from an argon atom to an alcohol ion is energetically impossible because the kinetic energies are only about 0.1 ev. This process is accompanied by the emission of a photon of 4.4 ev (difference of the ionization energies) which is quenched by the alcohol vapor. This effect has been investigated by Kallmann and Rosen,[18] who found that the cross section for electron transfer is of the order of magnitude of the gas kinetic cross section in the case of an ion beam moving through a gas of the same species. In the case of an ion beam moving through a gas of a different ionization potential, the cross section is somewhat less, but no appreciable number of argon ions can reach the cathode after $10^5$ collisions. In the commonly used self-quenching counters containing a mixture of gases, the ionization potential of the polyatomic constituent is invariably less than that of the inert gas. If the situation could be reversed, so that the inert gas has the lower ionization potential, then electron transfer would take place in the reverse direction and no polyatomic ions would reach the cathode. In such a counter photons would be quenched but not the secondary emission. The experimental tests to be described in the next section bear this out.

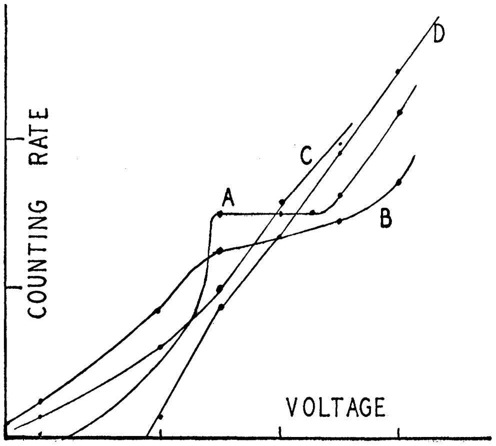

FIG. 1. Effect on plateau of methane counter produced by adding xenon. Curve *A*, pure methane; curve *B*, 0.3 mm of Xe added; curve *C*, 1.5 mm of Xe added; curve *D*, 1.5 cm of Xe added. Xenon has a lower ionization potential than methane, and consequently some xenon ions reach the cylinder where they produce secondary electrons and hence spurious counts. Methane pressure, 5 cm.

### EXPERIMENTAL TESTS

We have made some tests on counters containing methane with varying small amounts of a non-quenching gas of lower ionization potential. The gases used were xenon, air ($O_2$), and water vapor. The resistances used were $\frac{1}{4}$ megohm and other values down to 1000 ohms. With such low resistances a counter containing a pure non-quenching gas goes directly into a self-sustaining discharge with no Geiger region and without any appreciable region of proportional counting. A 9-cm $CH_4$+1-cm Xe counter, on the other hand, has a well-defined proportional region, as one would expect from the quenching of photons by the methane vapor. Figure 1 shows the counting rate *vs.* voltage curves for various mixtures of $CH_4$ and Xe. It is seen that the addition of 1.5 mm Xe to a $CH_4$ counter completely effaces the plateau. The oscilloscope shows that in place of a Geiger region there is a short voltage range between the proportional region and the self-sustaining discharge in which nearly every pulse is a multiple. From Fig. 1 we see that 0.3 mm of Xe is sufficient to alter the plateau substantially. This indicates that the presence of Xe (ionization potential 12.1 v) to one part in a thousand causes the production of an observable amount of secondary emission, manifested by multiple pulses and the resulting spurious counts which tilt the plateau. On the other hand, addition of 1.5 cm of argon whose ionization potential is 15.6 v (see Fig. 2) did not alter the flatness of

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[18] Kallman and Rosen, Zeits. f. Physik **61**, 61 (1930).

the plateau. Similar results were found for the methane-water vapor (Fig. 2) and methane-air (Fig. 3) mixtures, thus confirming the mechanism discussed previously. It is interesting to note that mercury vapor, which has a vapor pressure of $10^{-3}$ mm at room temperature, contaminates most counters to about one part in $10^5$ without affecting the plateau. Mercury has an ionization potential (10.4 v) less than that of methane (14.5 v). A methane counter containing a drop of mercury was totally immersed in a hot water bath, and it was observed that when the temperature rose to 82°C (vapor pressure of mercury 0.1 mm), the normal self-quenching action was destroyed. The tests on the triatomic gases, which showed no plateau when used with a $\frac{1}{4}$-megohm resistance, have been discussed in the previous section.

In all the experiments the counter used was 1.2 cm in diameter and 10 cm long, and had a 3-mil tungsten central wire. The counter was removed from the system, washed with acid, replaced, and baked under vacuum, and the wire was glowed between tests. The counting rates were observed with a 10-microgram radium source 12-cm distant, and were recorded on a scale of 64 counter. Each point on each curve represents between 2000 and 10,000 counts. The counting rate seldom exceeded 100 per second and was usually about 30 per second. It was therefore well within the resolving time of the counter. The voltages used ranged between 1000 and 1500. Neither the counting rates nor the voltages are numerically indicated in the figures since the quantities depend on the position of the radium source and the size of the counter and gas pressure, and hence their magnitude is not significant. For example, curves *A* and *B* in Fig. 2 have been separated to allow the plateaus to be inspected. Such a shift can be accomplished either by moving the source slightly or by shifting ordinates. The plateaus normally observed were about 50 volts long. A resistance of 250,000 ohms was used in all cases.

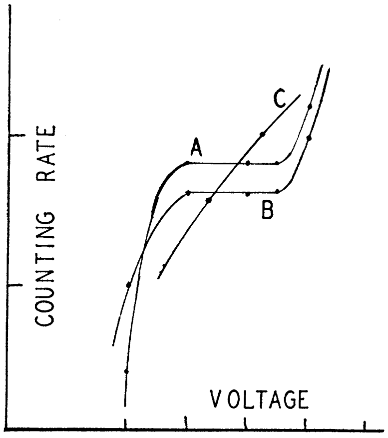

FIG. 2. Effect on plateau of methane counter produced by adding argon or water vapor. Curve *A*, pure methane; curve *B*, 1.5 cm argon added; curve *C*, 1.5 cm water vapor added. Note that the argon does not influence the flatness of the plateau while the addition of water vapor causes the plateau to disappear. The ionization potential of argon is greater than that of methane, while that of water vapor is less.

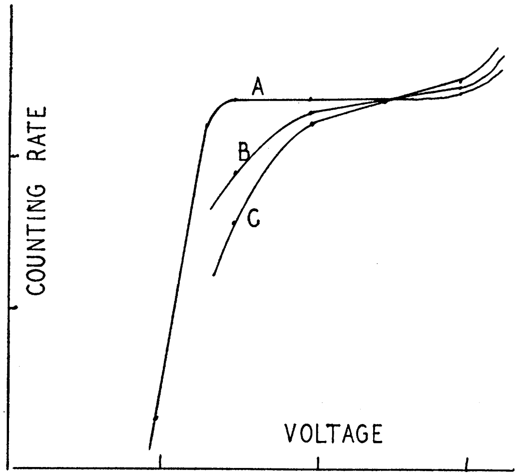

FIG. 3. Effect on plateau produced by adding air to a methane counter. Curve *A*, pure methane; curve *B*, 1.5 mm air added; curve *C*, 6 mm of air added. Methane pressure, 5 cm.

## APPENDIX: LINEAR VARIATION OF CHARGE WITH OVER-VOLTAGE

Stever[3] and Simpson[19] have found that the charge collected per count in a fast counter varies linearly with over-voltage except for high over-voltages. At the threshold of counting (starting potential), which we shall assume to be close to the threshold of the Geiger region, the most intense ionization of the avalanche occurs in the immediate vicinity of the wire where the field is

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[19] We are obliged to Dr. John A. Simpson for communicating to us some of his unpublished work.

about $10^5$ v/cm. Since the mean free path is $10^{-4}$ cm in a counter at 10-cm pressure, an electron near the wire can gain enough energy from the field between successive collisions to ionize. Let $E_c$ denote the critical field for intense ionization which is reached in the neighborhood of the wire (radius $r_w$) when the voltage is raised to the starting potential $V_s$. As the operating voltage $V$ is raised above $V_s$, the critical field moves out from the central wire, and if $r_c$ denotes the radius of the critical field and $c$ the capacitance per unit length of the counter, then $E_c=2cV/r_c=2cV_s/r_w$. It follows that $r_c-r_w$ is proportional to the over-voltage. Now the total number of electrons produced in the region of intense ionization is readily seen to be proportional to $\exp \int_{r_w}^{r_c} K(r)dr$, where $K(r)$ denotes the average number of electrons produced by ionization when one electron moves through unit distance. $K(r)$ is proportional to the ionization cross section which depends on the electron energy, which in turn depends on $r$. However, the energy loss through inelastic collisions is so great that the electron energy increases only slowly with decreasing $r$. For the electron energies attained in the region of intense ionization, the ionization cross section varies linearly with energy at first and then increases more slowly. Hence we may neglect the variation of $K(r)$ in the small interval over which the integral is evaluated. The charge collected per count is thus proportional to $\exp\{(r_c-r_w)/\bar{\lambda}_i\}$ where $\bar{\lambda}_i=1/\bar{K}$ = averaged mean free path for ionization. For the counters used $\bar{\lambda}_i \sim 10^{-2}$ cm and $r_c-r_w \lesssim 10^{-3}$ cm for not too high over-voltages. On expanding the exponential and neglecting powers of $(r_c-r_w)/\bar{\lambda}_i$ greater than the first, we obtain a linear dependence of the charge collected on $r_c-r_w$ and thus on $V-V_s$ which is the over-voltage. The more rapid rise of the charge collected at high over-voltages is essentially due to the sprays of multiple pulses. Toward the end of the Geiger region, an initial ionizing event will frequently produce a multiple instead of a single pulse. The charge collected increases with the frequency and multiplicity of the multiple pulses.