A Study of the Deterioration of Methane-Filled Geiger-Müller Counters

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The changes in the characteristics of methane-filled Geiger-Müller counters were studied as a function of counter life. It was found that the counters had a useful life of between 10^7 and 10^8 counts. Mass-spectroscopic analysis of the gas during the life of the counter showed the major decomposition products in the gaseous phase to be hydrogen, ethane, ethylene, and acetylene. These changes in gas composition did not account for the counter deterioration. The heavy hydrocarbon products deposited on the electrodes resulted in counter failure.

ONE of the well-known characteristics of Geiger-Müller counters which are filled with organic vapors for self-quenching action is the finite life for satisfactory counting behavior. Spatz[1] has obtained evidence of the decomposition of the gas in both argon-alcohol and argon-methane counters. The primary decomposition products were thought by Spatz to be 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 molecules are broken up and the end products of the decomposition are a non-quenching gas, such as hydrogen or oxygen, and heavy hydrocarbons deposited on the walls.

The observed life of methane counters is 10^7 to 10^8 counts, as against 10^{10} counts for an alcohol counter. Since CH_4 is one of the simplest hydrocarbons, it would be expected to decompose only once or twice before it is reduced to non-quenching diatomic molecules. In general, the number of molecules decomposed in each discharge will depend on the voltage. Thus, operating counters at voltages much above the discharge threshold will decrease the life. As the quenching constituent is decomposed, one might expect the total number of molecules in the counter to increase with a consequent increase in the pressure. Spatz reported such changes in both argon-alcohol and CH_4 counters. Concomitant with such changes in pressure, there would be an increase in starting potential, since this depends both on pressure and on the gas constituents.

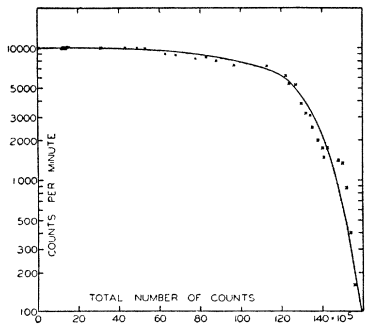

FIG. 1. The counting rate as a function of age for a methane-filled counter for which the applied voltage remains constant.

This paper reports a study of the life characteristics of methane-filled counters. Methane was chosen for two reasons: first, the gas is one of the simplest of the organic compounds suitable for counter filling, and second, detailed studies have already been carried out on the behavior of methane under ion bombardment and in gas discharges.

ELECTROCHEMICAL SUMMARY

Yeddanapalli[2] has made a detailed study of the decomposition of methane in glow discharges at liquid-air temperatures. He reports that the reaction products which are found are hydrogen, a polymer of composition CH_2, ethane, ethylene, and acetylene. The proportions of ethylene and acetylene increase as a result of the dehydrogenating action of atomic hydrogen; i.e., the atomic hydrogen dehydrogenates ethane or the radical fragments to give ethylene and this in turn reacts further to yield acetylene. Bimolecular combinations of the radicals formed by the

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

[2] L. M. Yeddanapalli, J. Chem. Phys. **10**, 249 (1942).

variety of collisions occurring in the gas phase and in the walls will lead to the formation of ethane, ethylene, and acetylene.

The hydrogen has two effects: first, it acts as a diluent, taking up a part of the electrical energy proportional to its partial pressure so that the rate of decomposition of CH_4 decreases in direct proportion to the partial pressure of H_2; and second, it acts as a dehydrogenating agent increasing the percentage of the unsaturated hydrocarbons in the reaction products. In a study of CH_4, C_2H_6, and C_3H_8, Bonhoeffer and Harteck[3] showed that atomic hydrogen reacts readily with hydrocarbon gases except methane, with the main reactions being hydrogenation, dehydrogenation and ring rupture.

Other studies of CH_4 in glow discharges at ordinary temperatures have been made. These report the formation of a wax-like, inert substance deposited on the cathode with the chief gaseous products being H_2, acetylene, ethylene, and paraffin hydrocarbons.[4] Numerous experiments on methane have been performed in different types of electrical discharges and under the action of alpha-rays,[5] and more recently under deuteron bombardment.[6] In general there is found H_2, saturated and unsaturated hydrocarbons in the gaseous products, and a solid or liquid residue. The heavier solid or liquid compounds are formed by polymerization of the unsaturated hydrocarbons, which takes place quite readily in the presence of H_2.

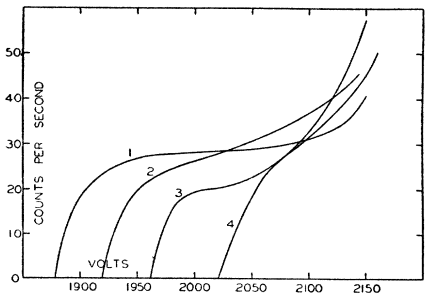

FIG. 2. Operating characteristics for a counter for various ages. Curve (1) was taken after 10^7 counts, (2) after 5×10^7 counts, (3) after 7×10^7 counts, (4) after 10^8 counts.

TABLE I. Summary of mass-spectroscopic results.

Counter	Total counts	H_2	C_2H_6	C_2H_4	C_2H_2	C_3H_8	C_4H_{10}
A	0	0	0.31			0.3	trace
	12.8×10^7	5.97	1.6	trace	0.32	0.6	0.3
B	0	0					
	0.92×10^7	1.5	0.5			trace	
	3.92×10^7	2.8	0.8	trace			
	7.02×10^7	4.5	1.5				
	43.3×10^7	14.0	1.9			trace	
C	14.5×10^7	13.0	1.9	trace		1.7	
D	2.5×10^7	1.54	0.3				
	5.0×10^7	3.1	0.6	trace			
	8.5×10^7	4.5	0.74				trace
	14.5×10^7	6.5	0.85				
	37.0×10^7	13.0	0.89			trace	

EXPERIMENTAL PROCEDURE

The experimental procedure in studying the decomposition products from aging methane gas in Geiger-Müller counters was as follows. The counters were filled with methane to some convenient pressure and operating potential, run at a suitable counting rate on a counting circuit, and samples of the gas were taken off at intervals. These samples were analyzed in a mass spectrometer.

The methane for the counters was purified before use in the following manner. The counters were connected to a vacuum system manifold which was evacuated with a mechanical pump. Tank methane was admitted to the system and frozen into a trap at liquid nitrogen temperature. With boiling nitrogen on the trap, all fractions of the gas except nitrogen, oxygen, and 4 mm pressure of methane (the vapor pressure of CH_4 at liquid nitrogen temperature) were frozen in the

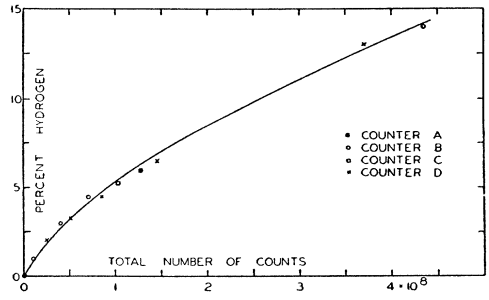

FIG. 3. The build-up of hydrogen gas with age for methane-filled counters is plotted for the counters of Table I.

[3] K. F. Bonhoeffer and P. Harteck, Zeits. f. physik. Chemie, **139**, 75 (1928); Zeits. f. Elektrochemie **34**, 652 (1928).

[4] W. D. Harkins and J. M. Jackson, J. Chem. Phys. **1**, 37 (1933); E. G. Linder, Phys. Rev. **36**, 1375 (1930); E. G. Linder and A. P. Davis, J. Phys. Chem. **35**, 3649 (1931).

[5] S. C. Lind, *The Chemical Effects of Alpha Particles and Electrons* (The Chemical Catalogue Co., New York, 1928) p. 146.

[6] R. E. Honig, C. W. Sheppard, J. Phys. Chem. **50**, 119 (1946).

trap. These impurities were pumped off. The trap bath was then changed to liquid oxygen and the gas system was allowed to build up to the vapor pressure of CH_4, which is 8 cm pressure at liquid oxygen temperature. This purified methane was then used for the counter filling.

Before loading, the counter tubes were outgassed to drive off absorbed gases in the metal and glass walls, and the center wire was flashed for several minutes. The counters were filled to a pressure of 6 cm of mercury.

To the experimental counters were attached a number of glass bulbs with internal break-off seals for collecting samples of the gas. The take-off bulbs had an average volume of 20 cubic centimeters and the volume of the counters was 100 cubic centimeters.

All the analytic work on the gas samples was carried out on a 60° Nier-type mass spectrometer. The gas was allowed to expand into a large reservoir and there flow through a suitable leak into the ionization region of the spectrometer. Here excitation and ionization of the gas molecules were produced by electron impact. After acceleration by variable electric fields, a fraction of the ionized molecules, collimated by several slits to form an ion beam, was analyzed by a magnetic field. The components of the resulting mass spectrum were measured electrically by the collector connected to an FP-54 d.c. amplifier circuit.

The counters were aged by operating them continuously on an ordinary amplifier and scaling circuit. The resistance in series with the counter center wire and the high voltage supply was 10^6 ohms. The counters were run at a rate of about 10^4 counts per minute, giving aging periods of one or two weeks.

RESULTS

The changes in the electrical characteristics of methane counters caused by the decomposition of the filling gas are easily measurable. When such a counter is connected to a constant voltage and data are taken of the observed counting rate as a result of a constant radioactive source as a function of time, it shows a typical behavior, illustrated in Fig. 1. The counting rate is quite constant up to about 10^7 counts, and then the sensitivity drops rapidly. Representative plateau curves are shown in Fig. 2. One can see that the primary reason for the decrease in sensitivity shown in Fig. 1 is the increase in threshold voltage. The aging data for this investigation were taken by keeping the counting rate constant. This was done by increasing the operating voltage to compensate for the rising threshold voltage. From the curves of Fig. 2, it is obvious that the rising threshold is not the only aging effect. The plateau curves become both narrower and steeper and a point is finally reached when the characteristics become so poor that no further operation as a Geiger-Müller counter is possible.

A summary of the mass spectroscopic results is given in Table I. Preliminary runs, of which counter *A* in this table represents an example, showed that the principal decomposition product was hydrogen. The next most abundant product was ethane. Since ethane itself is known to be a good counter-quenching gas and the other products appeared in such small quantities, the principal accuracy of the spectrometer was directed toward the determination of the hydrogen fraction. From the data in Table I, we have plotted in Fig. 3 the percentage of hydrogen formed as a function of the total number of counts. This logarithmic increase in hydrogen concentration with number of counts extends up to the point where the counter could no longer be operated in its Geiger-Müller region. Counter failure occured in all cases for hydrogen concentrations between 13 and 14 percent. In no case do we even approach complete disintegration of the methane molecules. The end products are undecomposed CH_4 molecules, the non-quenching gas hydrogen, slight amounts of saturated hydrocarbons up to C_4H_{10}, ethylene and acetylene.

To determine whether this changing gas concentration could account for the counter failure, a clean counter was filled with 13 percent H_2 and 87 percent CH_4. The plateau characteristics of this filling were identical with the same counter filled with 100 percent CH_4. As a further check to see whether the gas filling was responsible for the counter failure, immediately after a counter had deteriorated it was put on the vacuum system, evacuated and refilled with freshly purified methane. The counter exhibited no better proper-

ties with the fresh methane filling than it did with the methane plus decomposition fragments present.

It was found that after a methane counter had deteriorated it could always be recovered by a thorough cleaning of the electrodes. Usually washing the counter very thoroughly with distilled water, alcohol, benzene, and ether was sufficient. Occasionally a counter did not respond to this treatment, and in these cases, removal of the anode wire showed it was covered with a heavy brown coating which on heating left a carbon black on the wire.

CONCLUSION

The results of these experiments show that methane Geiger-Müller counters deteriorate because of the decomposition of the gas and that the change in the gas composition does not lead to the counter failure. The counter deterioration can be explained by the heavy hydrocarbon decomposition fragments of the methane deposited on both the cathode cylinder and on the anode wire.

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The Factorization Method, Hydrogen Intensities, and Related Problems

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The factorization method enables us to calculate in an elementary way the discrete-discrete and discrete-continuous transition probabilities of hydrogen atoms by means of recurrence formulae. From a key intensity all others are found by a repeated application of an l-changing recurrence formula or an n'-changing operator. The results are given:

for l-changing in the formulae: (4.2), (4.3),
for n'-changing in the formulae: (5.1), (5.2) with (3.2).

Some of the formulae apply to more general matrix components.

I. INTRODUCTION

THE value of the Schrödinger hydrogen intensity integral

$$I_{n'\,n}{}^{l-1\,l}=\int_0^\infty rR_{n'}{}^{l-1}R_n{}^l dr, \qquad (1.1)$$

(where $R_n{}^l=r$ times the Schrödinger normalized hydrogen radial function) has been calculated many times. Originally Schrödinger[1] calculated it for special cases using the generating function for Laguerre polynomials. Wheeler[2] has recently applied this method to the general case of discrete-discrete transitions. Epstein[3] used the theory of hypergeometric functions to solve the same problem, while Eckart[4] evaluated the integral directly. Gordon[5] has treated the discrete-continuous and continuous-continuous as well as the discrete-discrete transitions. We want to show that the factorization method leads to a simple treatment of this problem.

The factorization method gives the *solutions* of a second-order differential equation by means of recurrence formulae[6]; the idea here is to develop recurrence formulae for the integrals involving these solutions—the intensity integral in particular. Besides the recurrence formulae a starting point is needed; in what follows this is found by the method of the Laplace transform. Some of the formulae apply to the calculation of other integrals involved in the Kepler problem.

[1] Schrödinger, *Wave Mechanics* (Blackie & Son, London, 1928), p. 99.
[2] Wheeler, Proc. Roy. Irish Acad. **50**, Sec. A, 3 (1944).
[3] Epstein, Proc. Nat. Acad. Sci. **12**, 629 (1926).
[4] Eckart, Phys. Rev. **28**, 927 (1926).
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[6] L. Infeld, Phys. Rev. **59**, 737 (1941).