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CONTINUOUS PURIFICATION OF HYDROGEN AND ARGON-HYDROGEN GAS MIXTURES

by

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CONTINUOUS PURIFICATION OF HYDROGEN AND ARGON-HYDROGEN GAS MIXTURES

By Ernest D. Klema

ABSTRACT

A method for the continuous convection-current purification of hydrogen and argon-hydrogen gas mixtures is described. Three substances have been used successfully as purifying agents. The electron drift velocity in argon-hydrogen mixtures should be high compared to the drift velocity in pure argon.

* * * * *

The use of metallic calcium in convection-current argon purifiers has been described previously, and the method has been used successfully in this laboratory.* The method proposed at the same time for the purification of hydrogen and argon-hydrogen mixtures, using platinized asbestos and a desiccating agent, is not convenient to use; furthermore it has been shown by recent work that it is not so effective as the new method to be described in the following pages.

Some work has been done in this laboratory on a chamber filled with hydrogen and argon which utilizes electron collection on a small central wire, for use as a neutron spectrometer. The response of this counter did not stay constant with time. It was thought that changing purity of the gas mixture was responsible for this effect, and that a means of continuously purifying it was needed.

The following setup was used to test the effectiveness of several possible methods of purification. A chamber with 3-inch outside diameter and 25-mil center wire was provided with fittings and a purifier to allow gas to circulate through it. The purifier was connected to the chamber with long saran leads, both for insulation and for the reason that saran has been shown to be bad from the standpoint of giving off vapors which seem to capture electrons markedly. If a method works in this case, it should work for any type of chamber construction. Figure 1 shows a schematic drawing of the setup.

A thin electroplated foil of Pu, prepared by Sgt. Miller, which emits about 5000 alpha particles per minute, was placed on the inner wall of the cylinder. The pulses from the chamber were amplified by means of a Model 100 Sands amplifier with a short time constant of 80 microseconds and then fed to two discriminators connected in parallel. The bias of one discriminator was kept fixed, and integral bias curves were obtained by varying the bias of the other discriminator and observing the number of counts at each bias for a given number of counts on the fixed-bias channel. In all cases the bias curve had a definite slope due to the fact that the Pu foil was fitted against the curved inner wall of the cylinder.

The purifier used was one of the standard type which is used by the W group for the purification of argon. The temperature of the purifier was measured by means of a mercury-in-glass thermometer placed next to a thin layer of asbestos tape wound around the Kanthal heating coil. There was one layer of this asbestos tape between the coil and the steel purifier, and many layers of thick tape outside

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* Physical Review 63:18 (1943).

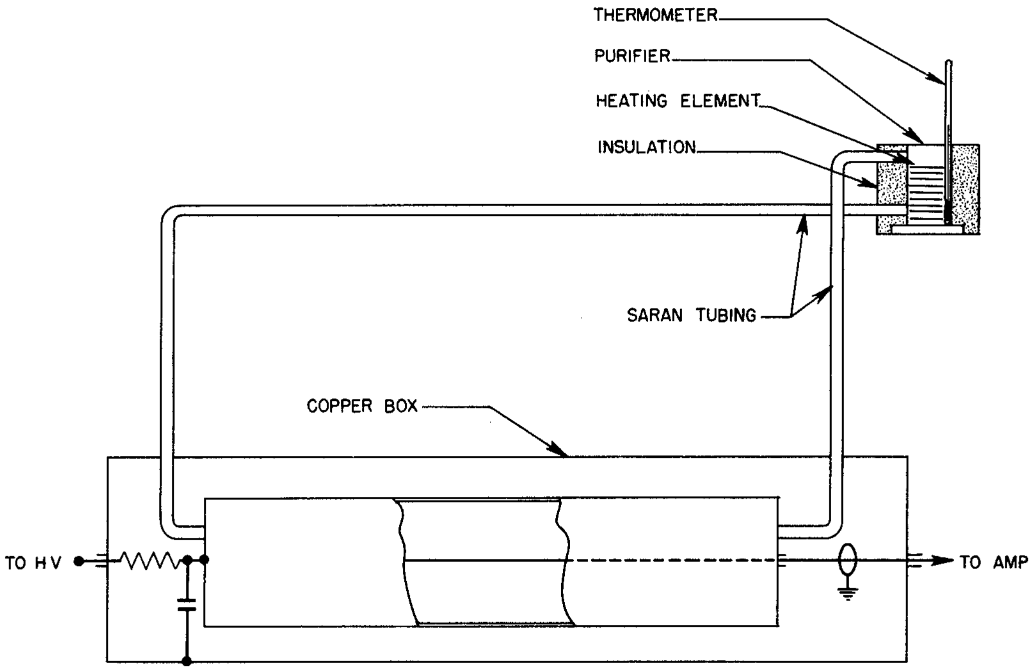

Figure 1. Schematic drawing of purification chamber.

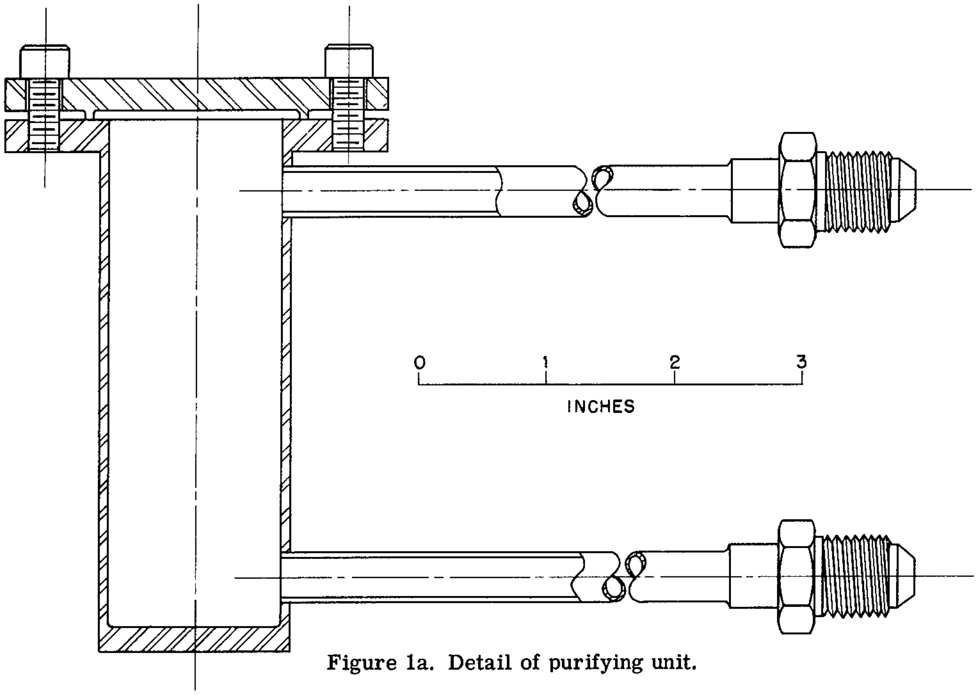

Figure 1a. Detail of purifying unit.

the thermometer. For each new filling of gas the system was evacuated and the purifying agent was outgassed at approximately the temperature at which it was to be used. Figure 1a shows the purifier in greater detail.

The system was filled initially with 3 atmospheres of 99.6% argon and then with a mixture of 1 atmosphere of tank hydrogen and 3 of 99.6% argon to provide a basis of comparison with the same gases when purified later. With the argon, pulses were obtained with 100 volts across the chamber. They increased in size with voltage up to about 1000 volts, and then showed no further increase. With the mixture of hydrogen and argon, no observable pulses at all were obtained until the voltage was raised to about 1500 volts. Their size increased with increasing voltage up to the limit of the battery pack used, 2975 volts. No bias curves were taken with the unpurified mixture because of the very high voltage required for any pulses at all.

The first attempt at purification was made using metallic magnesium in the purifier. The gas filling was 3 atmospheres of 99.6% argon, and 1 atmosphere of tank hydrogen. It was found that the magnesium was ineffective at a purifier temperature of 250°C, apparently because it had protectively oxidized and would not oxidize further. To overcome this difficulty, the surface of the magnesium was etched by placing it in dilute hydrochloric acid, and the metal surface thus exposed was protected from oxidation by rinsing immediately in distilled water and then in alcohol and then placing the magnesium in the purifier and evacuating the system before the alcohol had time to evaporate. When this was done, the pulse height increased over the value obtained with the tank gas and stayed constant for a few hours. Then it decreased again, probably because all the new surface had been used up and then the reactions ceased.

The possibility of heating the magnesium to a point near enough to its melting point to make it flow and thus expose new surface was tried next. The temperature of the purifier with a filling of magnesium just as it comes from the can was raised in 50-degree steps. At a temperature of 500 degrees, the purifier became effective and the pulse height increased to the value observed for the short time previously. The apparatus operated continuously for 4 days, with the pulse height remaining at the correct value. Upon examination at the end of that time, it was found that the magnesium had vaporized and then condensed on the walls of the purifier and in the tubes leading from it. The tubes were not at all seriously clogged at the end of this time, but one might run into difficulty from this source if the purifier were run continuously for considerably longer periods of time.

Next a filling of calcium hydride was tried with the same mixture of hydrogen and argon in the hope that it might be an effective purifying agent at a temperature lower than that necessary when using magnesium. The calcium hydride was obtained from Metal Hydrides Incorporated, and was between −4 and +8 mesh in size. It worked very well at 250 degrees; the pulse height rose to the correct value in 1 hour and remained there for the length of the test, in this case 3 days. Upon opening the purifier, it was found that only a very small fraction of the calcium hydride had been oxidized and that the purifier could have been operated continuously for an indefinite length of time. The calcium hydride oxidizes extremely rapidly in air, a chunk becoming powder in a half-hour, so that one must be careful to expose it to air only for very short times. The bias curves obtained at different collecting voltages with this purifying agent are shown in Figure 2.

In connection with some other work, it was useful to compare the voltage necessary to saturate the purified mixture just described with that necessary to saturate pure argon of the same stopping power. Metallic calcium was used in the purifier, and it was found that no saturation exists for the geometry used in the case of the pure argon. Apparently, when the field strength near the wall is still too low to saturate the alpha-particle ionization, the field strength near the wire is already high enough to cause multiplication. With this pure argon filling, the counter was very unstable and good reproducibility of bias curves was not obtained. The curves which were obtained are shown in Figure 3.

One method of getting around this difficulty is to keep the average energy of the electrons down by introducing a small amount of hydrogen into the chamber. A convenient way of accomplishing this is to make use of the equilibrium vapor pressure of hydrogen over calcium hydride. To test this idea,

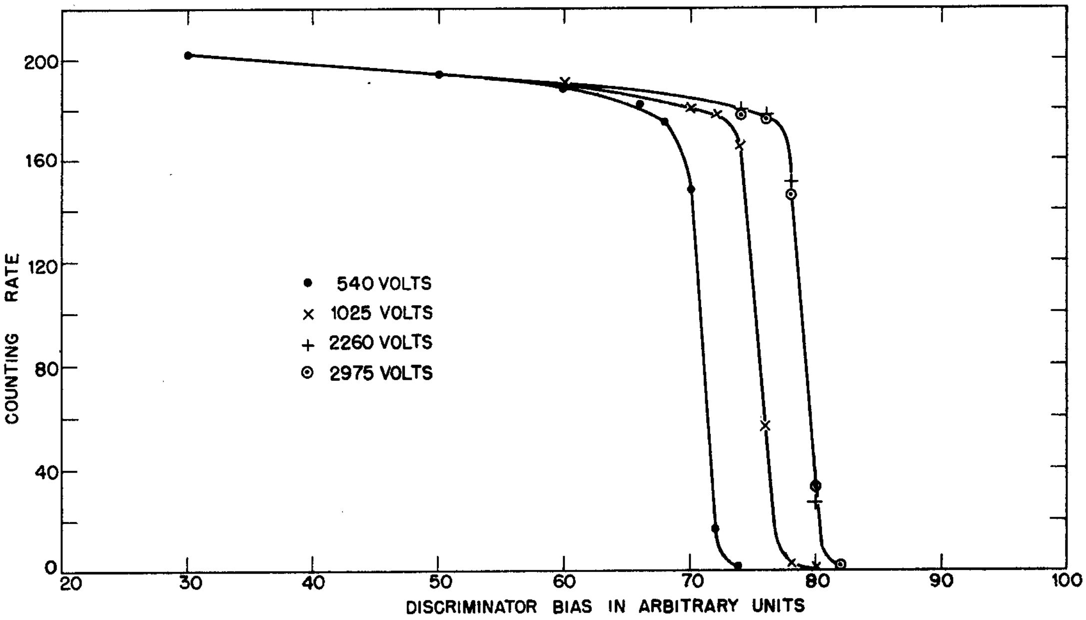

Figure 2. Bias curves obtained at different collecting voltages with H_2-A gas mixture and CaH_2 as the purifying agent.

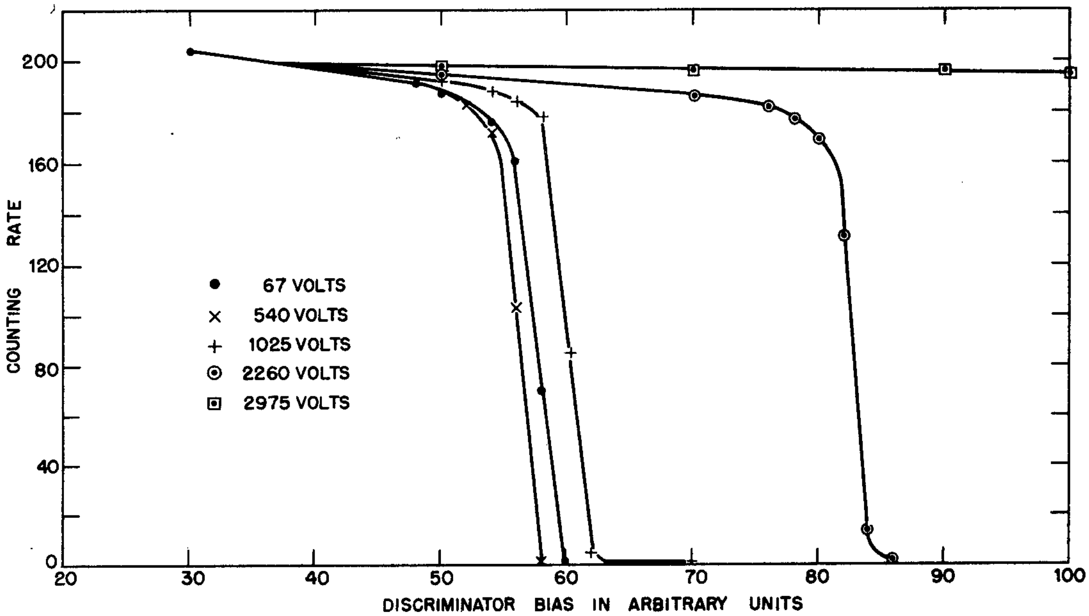

Figure 3. Bias curves obtained with pure argon.

the purifier was filled with calcium hydride and a few pieces of metallic calcium, and the system was filled with 35 pounds gauge pressure of argon. The temperature of the purifier was raised in steps to find the minimum temperature and amount of hydrogen necessary to eliminate the multiplication. It was found that when the temperature was 480 degrees or above, the bias curves remained unchanged with time. The highest temperature used was 525 degrees. The voltage necessary to saturate the ionization in this case was much lower than that necessary for the mixture of 3 atmospheres of argon and 1 of hydrogen, quantitative comparison being made impossible by a breakdown of the apparatus. The bias curves obtained are shown in Figure 4.

The apparatus was repaired, and an attempt to reproduce the foregoing data was unsuccessful. Upon investigation it was learned that the vapor pressure of hydrogen in this case is not the pressure corresponding to equilibrium among the three constituents, calcium hydride, calcium, and hydrogen. Rather calcium hydride and metallic calcium form a series of solid solutions with the dissociation pressure being dependent upon the composition of the condensed mixture.* The calcium hydride made by the Metal Hydrides Corporation varies between 90 and 95 per cent purity, and in this range of composition the equilibrium vapor pressure of hydrogen rises quite rapidly with increasing purity of the hydride. It may be possible to obtain reproducible results by allowing a fixed pressure of hydrogen to remain in the purifier for a given time each time the chamber is evacuated and filled with new gas, but a few trials in this direction were not entirely successful.

A difficulty encountered in this work with calcium hydride was the fact that particles from the purifying agent were carried by the convection current into the chamber when high purifier temperatures were used. It was found sufficient to remedy this condition to blow argon or nitrogen through the purifier until no more dust came out before it was connected to the system. It would probably be advisable to install a baffle between the upper lead of the purifier and the chamber to eliminate the possibility of dust being carried into the chamber by the gas.

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* Journal of the American Chemical Society 61:318 (1939).

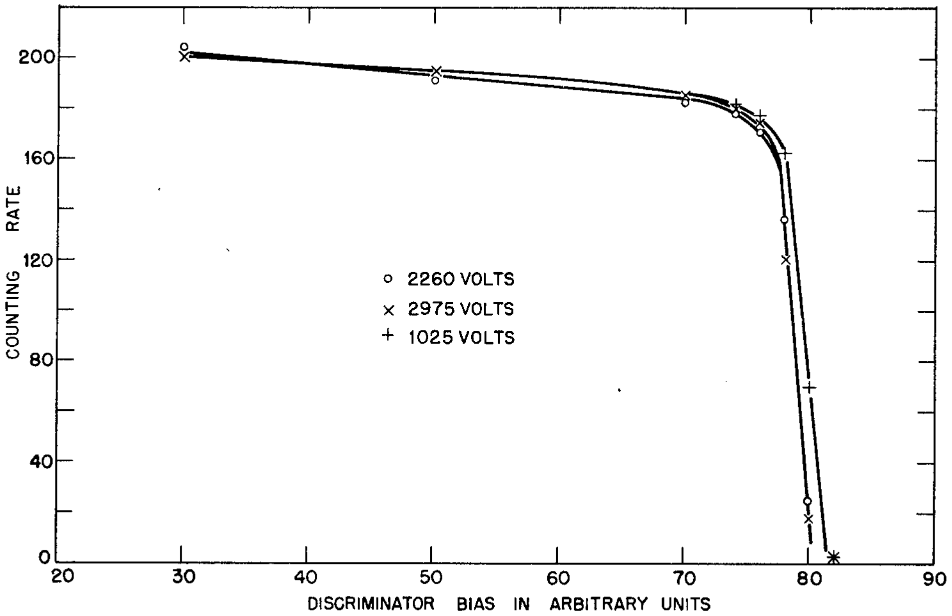

Figure 4. Bias curves obtained with the procedure described at the top of this page.

Titanium hydride was also used as a purifying agent. Since it can be obtained from the Metal Hydrides Corporation in 200-mesh particle size only, it was pressed with an equal weight of powdered magnesium and then broken up into lumps of convenient size for use in the purifier. The titanium hydride also purified mixtures of hydrogen and argon successfully at 250 degrees. Rough measurements on its equilibrium vapor pressure as a function of temperature showed that hydrogen is evolved from it in appreciable amount at lower temperatures than in the case of calcium hydride, and that its vapor pressure is considerably higher at corresponding temperatures. Again, data of good reproducibility were not obtained.

Because of the fact that the presence of hydrogen in argon-hydrogen mixture lowers the average energy of the electrons, one would expect the drift velocities of electrons in such mixtures to be considerably higher than the drift velocities in pure argon since the drift velocity is an inverse function of the random velocity.* Thus the pulses from electron-collecting ion chambers should rise more rapidly when the chamber is filled with purified argon-hydrogen mixtures than when it is filled with pure argon alone. Qualitative results have been obtained which show that this is the case, but no quantitative measurements have been made.

It would be of interest to measure the rise time of pulses in a chamber as a function of the percentage of hydrogen in an argon-hydrogen mixture, and to compare the values with the rise time in the case of pure argon. Since we have shown that it is easier to saturate mixtures with very small amounts of hydrogen than those with large amounts, it would be useful to know the minimum amount of hydrogen necessary to increase the drift velocity to a given value.

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