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MEASUREMENT OF THE PERMEABILITY OF METALS TO HYDROGEN AT ROOM TEMPERATURES

A. H. DEXTER

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Savannah River Laboratory

Aiken, South Carolina

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MEASUREMENT OF THE PERMEABILITY OF METALS TO HYDROGEN AT ROOM TEMPERATURES

by

Arthur H. Dexter

Approved by

P. H. Permar, Research Manager
Nuclear Materials Division

April 1968

E. I. DU PONT DE NEMOURS & COMPANY
SAVANNAH RIVER LABORATORY
AIKEN, S. C. 29801

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ABSTRACT

Previous measurements of hydrogen permeation of metals have been limited to high temperatures where permeation rates are relatively high and pressure-sensing devices can be employed to measure the permeating gas. Permeation rates at room temperature can be measured by the use of tritium (the radioactive isotope of hydrogen) and conventional counting equipment. With the equipment and techniques described in this report, it is possible to measure hydrogen permeation rates on the order of 10^{-17} cm^3 (STP)/(sec)(cm^2) per mm thickness of metal.

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INTRODUCTION

Certain metals are adversely affected by exposure to hydrogen. The migration of hydrogen into the metal is referred to as permeation, a term which includes sorption of hydrogen molecules at the gas-metal interface, dissociation of the molecules into atoms, and the subsequent diffusion of the atoms through the bulk of the metal. At another interface, recombination and desorption may also occur as part of the total process of permeation. Knowledge of the rate of hydrogen permeation in metals is important to the prediction of both hydrogen content and the effect of the contained hydrogen on the mechanical properties of the metal. The degree of deleterious effects, such as losses in ductility or static load-bearing ability, usually depends on the amount of hydrogen that enters the metal.

Almost all permeation data reported in the literature have been obtained at temperatures in excess of 250°C. At these temperatures, the permeation rates are relatively high, and as a consequence the rate of permeation can be conveniently measured by exposing one face of a metallic membrane to hydrogen and measuring the increase in gas pressure at the opposite face as a function of time. Conventional laboratory equipment is readily applicable to such measurements.

Because the rate of permeation is an exponential function of temperature, a considerable extrapolation of existing data is required to obtain rates at room temperature. Moreover, limited data at room temperature indicate that extrapolated rates may be in error by factors on the order of 100 to 10,000,[1] perhaps because surface effects would be expected to have greater influence on permeation rates at room temperature.

At room temperatures, permeation rates on the order of 10^{-13} to 10^{-20} cm^3/sec of hydrogen per cm^2 of metallic surface and mm thickness are expected. Mass spectrometers and conventional PVT measurements are no longer applicable. Other measurement techniques that will provide the requisite sensitivity are described in this report.

SUMMARY

Radiotracer techniques were successfully applied to measure the hydrogen permeation of metals. By incorporating tritium (H^3) in the hydrogen to which the metal specimen is exposed, permeation rates on the order of 10^{-17} cm^3/sec per cm^2 can be measured.

The quantity of tritium permeating a metallic specimen in a given time is determined by means of proportional counters. Because of the low penetration power of the beta particles emitted by tritium, it is necessary to introduce the tritium directly into a counter. This is readily accomplished by enclosing the permeation specimen in a secondary container which in turn is directly connected to a proportional counter.

This report describes both the equipment and techniques for the determination of very low permeation rates at room temperatures. The method provides an opportunity to study permeation at room temperatures as well as to study the surface phenomena that may be limiting at these temperatures.

DISCUSSION

Tritium is an ideal tracer for studies of the hydrogen permeation of metals at room temperature. Tritium is readily available from the Oak Ridge National Laboratory at a price of $2 per curie.[2] The amount required will be a function of both the geometry of the permeation specimen and the efficiency of the tritium-counting system. With judicious design, essentially pure tritium can be used at a reasonable cost. As an example, permeation specimens consisting of metallic membranes with an area of 100 cm^2 and a nominal thickness of 0.7 mm were backed by 14 cm^3 of essentially pure tritium. The counting efficiency of the system employed was nominally 41%. Since tritium at STP has a concentration of 2.5 $curies/cm^3$, the cost of the tritium employed was about $73 per specimen. Permeation rates as measured with these specimens were on the order of 10^{-15} cm^3/sec per cm^2 of area.

Tritium permeates metals at essentially the same rate as hydrogen. Only one investigation[3] has been made of an isotopic effect on permeation rate and this involved the permeability of 347 stainless steel at high temperatures with rates measured by PVT methods. The results indicate that the ratio of hydrogen to tritium permeation is $\cong 2$ and not greatly different from the inverse ratio of the square root of their masses, i.e. $\sqrt{3} = 1.732$. With this correction, reasonable accuracy can be assumed.

The permeation measurement system, as shown schematically in Figure 1, is basically a closed loop consisting of three interconnected units: a flow-through proportional counter, a recirculating pump, and a permeation specimen that is enclosed in a secondary container. This system is filled with a nuclear counting gas* consisting of 90% argon and 10% methane, which the proportional counter requires. The permeating gas and the P-10 are mixed with a small recirculating pump. The system can be evacuated with the vacuum pump prior to a permeation-rate measurement and refilled with fresh P-10 from a tank or other source of supply.

The beta particles resulting from the radioactive decay of tritium in the proportional counter produce small voltage pulses at the output of the proportional counter, which are subsequently amplified and counted with a scaler.

A more detailed description of pertinent equipment follows.

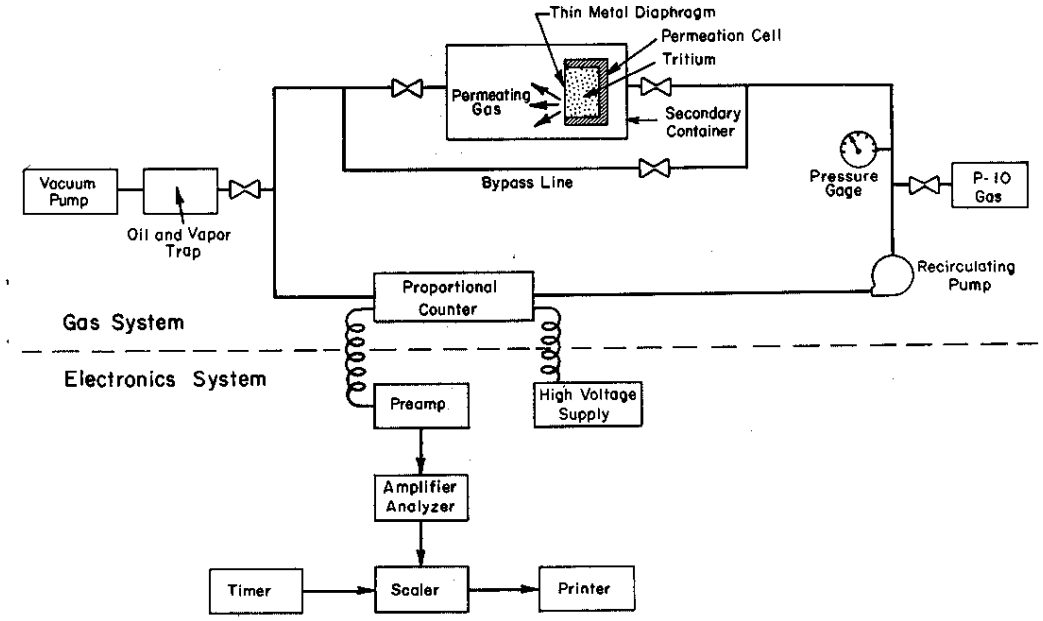

FIG. 1 SCHEMATIC DIAGRAM OF PERMEATION-RATE MEASUREMENT SYSTEM

* Referred to as P-10 counting gas and available from the Matheson Company, Inc.

PERMEATION-RATE MEASURING EQUIPMENT

The flow-through proportional counter constructed at the Savannah River Laboratory (SRL) is similar in design to one[4] employed by Hanna and Pontecorvo[5] for tritium studies. Basically the counter is a pipe with an ID of one inch and a length of 12 inches. Glass-to-metal seals (Figure 2) are brazed into each end of the pipe. These seals support a .003-inch axial wire of tungsten that is held taut by a small phosphor bronze spring at one end (Figure 3). Welded inlet and outlet pipes are positioned so that the flow does not impinge directly on the axial wire; this avoids undesirable vibrations of the wire. Information on both design and construction techniques can be found in standard references.[5,6]

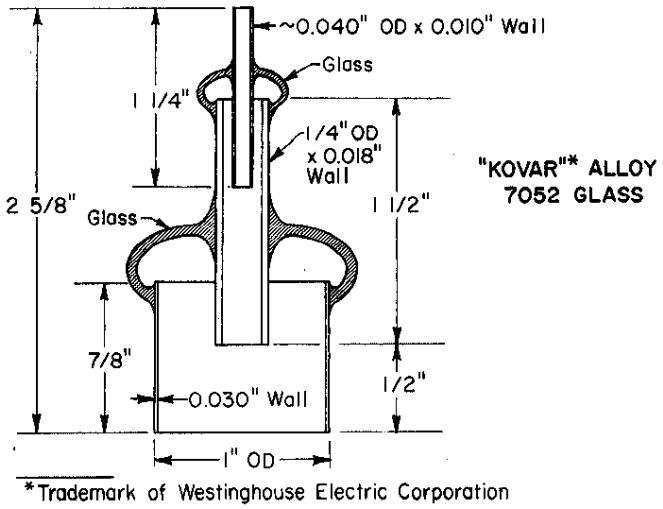

FIG. 2 GLASS-TO-METAL SEAL USED IN PROPORTIONAL COUNTER

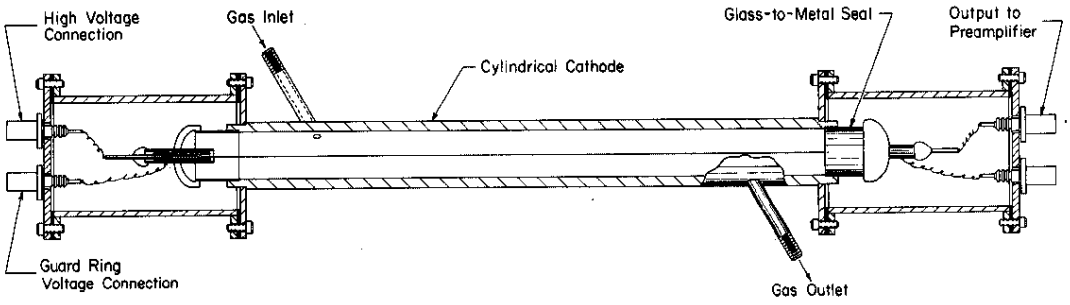

FIG. 3 FLOW-THROUGH PROPORTIONAL COUNTER

P-10 counting gas is used because it is the only proportional gas filling that provides output pulses, which are proportional in amplitude to the energy of the betas producing the pulses. An operating pressure of 540 mm of Hg is employed. The recirculating pump is a Neptune Dyna-Pump (Model 2), with a "Viton"* diaphragm.

The preamplifier is a solid-state device fabricated at SRL (Figure 4). Nuclear-Chicago Corp. (RIDL) counting equipment is used, but other manufacturers provide comparable equipment. The amplifier/analyzer is a Model 33-13A, the scaler is a Model 49-28, and the timer is a Model 54-7. In recent times automatic readout has been added by the substitution of a Model 49-44 printing scaler and a Model 54-8 timer, and by a Hewlett Packard, Model 44-21 printer. The high voltage for the proportional counter is provided by a Model 412B High Voltage Supply, John Fluke Mfg. Co. An operating voltage of 1750 volts is used for the proportional counter employed.

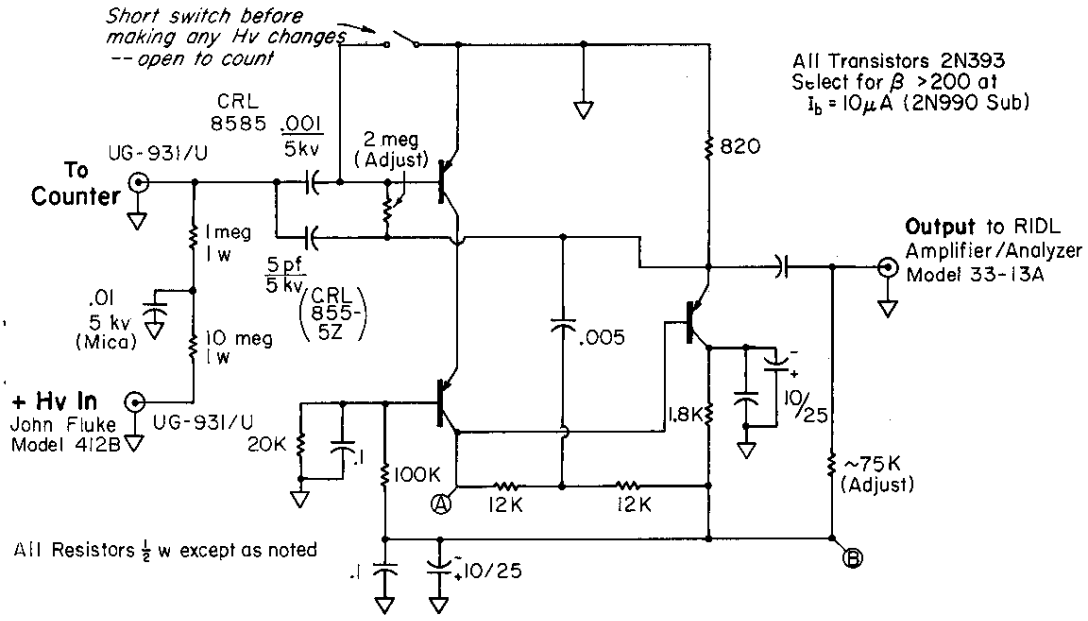

FIG. 4 CHARGE SENSITIVE PREAMPLIFIER FOR PROPORTIONAL COUNTER

* Du Pont's trademark for fluoroelastomer.

MEASUREMENT PROCEDURE

Determination of Discriminator Setting for Operation

Prior to the use of the equipment for a permeation measurement, a loop of tubing (i.e., a bypass line) is employed in place of a permeation specimen and the count rate of the "clean" system is determined as a function of the dial setting of the integral discriminator on the amplifier/analyzer. The results (Figure 5) show that for a discriminator setting of 60 divisions the pulses due to electronic "noise" from the preamp will be eliminated. This discriminator setting is used then for all permeation measurements.

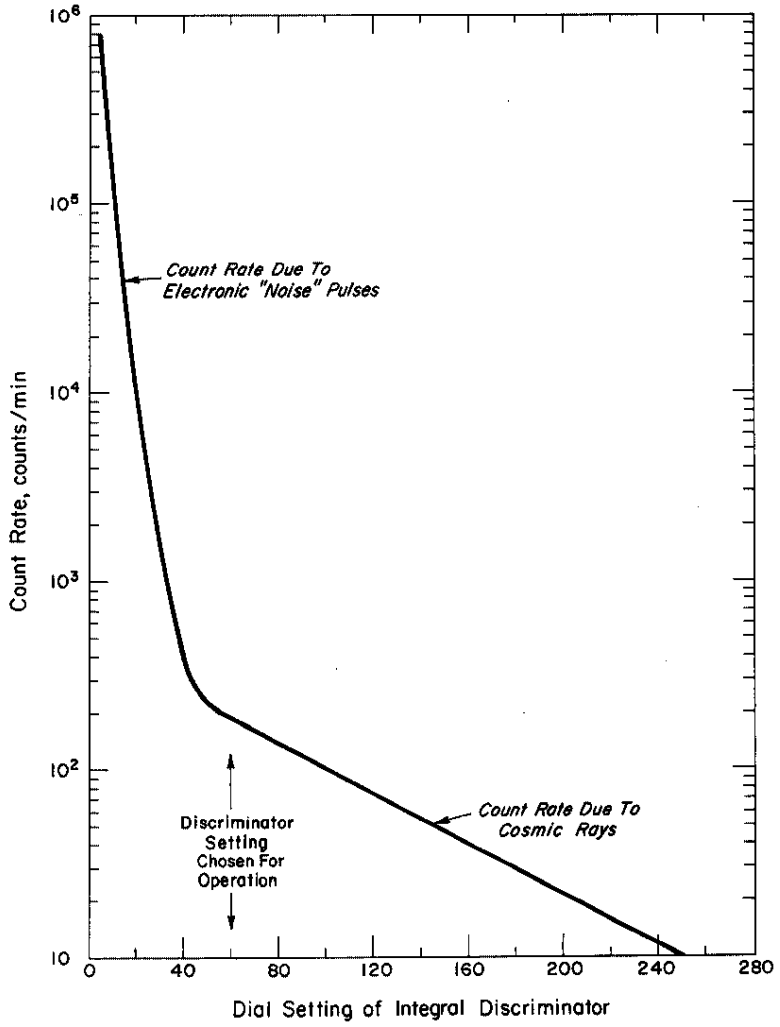

FIG. 5 COUNT RATE vs DISCRIMINATOR SETTING FOR "CLEAN" SYSTEM

Permeation Measurement

With the permeation specimen connected to the system, the system is alternately evacuated and flushed to remove as much residual tritium as possible. Finally P-10 is admitted to a pressure of approximately 540 mm of Hg, and the secondary container that houses the permeation specimen is valved off and allowed to collect the permeating gas for some period of time (t'). During this collection period, the background count rate (B) of the system is determined. This background activity is due to cosmic rays and residual traces of tritium.

At the end of the collection time (t'), the secondary container is valved in. The count rate increases almost immediately due to the tritium that has permeated the specimen and collected in the secondary container. Thereafter, the count rate continues to increase with time (t) since the permeation specimen is adding additional tritium to the system at the permeation rate, P (cm^3/min). It can be shown that the count rate (dc/dt) at any time (t) after valving in the specimen is:

$$\frac{dc}{dt} = APt + APt' + B$$

where $\frac{dc}{dt}$ = count rate, counts/min

$$A = \frac{2.6 \text{ curies}}{cm^3} \times 3.7 \times 10^{10} \frac{\text{disintegrations/sec}}{\text{curie}} \times \text{system counting efficiency (counts/disintegration)}$$
$$= (\text{counts}/(\text{sec})(cm^3))$$

P = permeation rate, cm^3/min

t = time after valving in specimen, sec

t' = collection time, sec

B = background count rate, counts/min

Thus a plot of count rate ($\frac{dc}{dt}$) vs. time (t) is, in theory, linear with a slope of AP and an intercept of (APt' + B) on the ordinate at t = 0. This idealized situation is shown in Figure 6. In practice, due to time lags involved in the mixing of the tritium (after valving in), and/or the vagaries of gas dynamics, it is possible to obtain data plots as shown in Figure 7. The same analysis of the data is applicable to both of these situations by extrapolation of the linear slope back to t = 0.

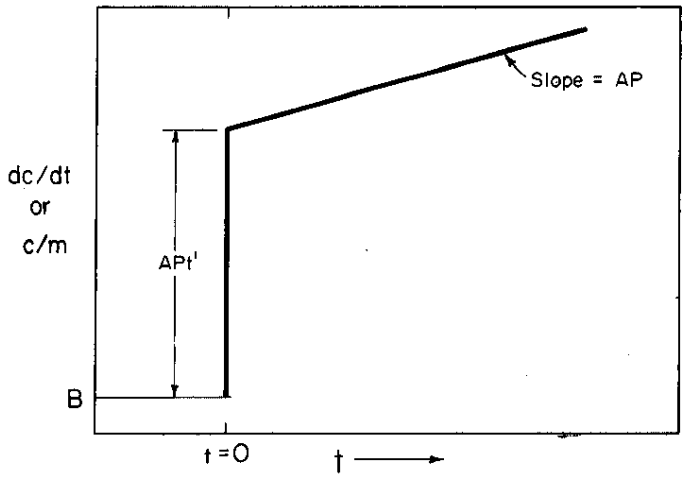

FIG. 6 THEORETICAL PREDICTION OF dc/dt vs TIME

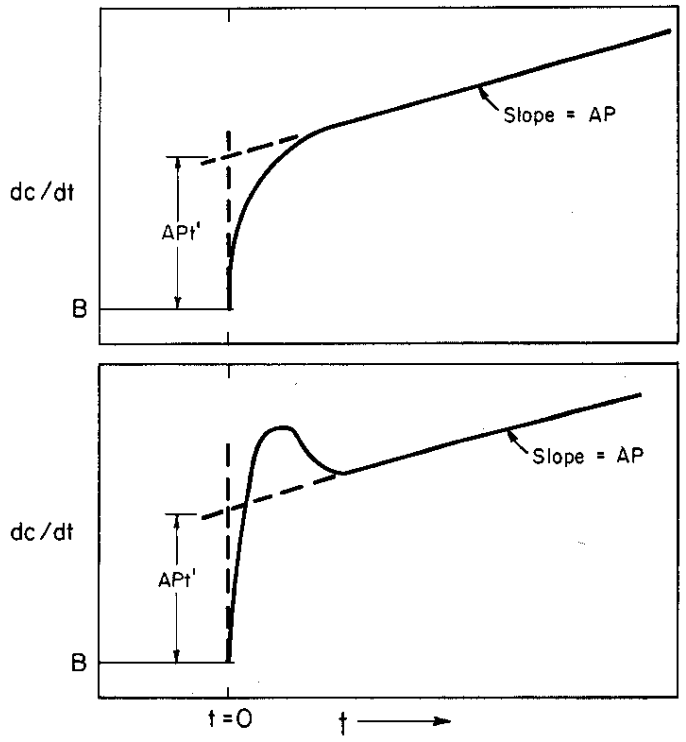

FIG. 7 PLOTS OF dc/dt vs t OBTAINED IN PRACTICE

Determination of System Counting Efficiency

At the conclusion of the permeation measurement, it is necessary to determine the counting efficiency of the system. The efficiency of the counter is first established by measuring count rate vs. discriminator setting. In Figure 8, a discriminator setting of 575 divisions results in the elimination of counts due to the tritium betas, and only cosmic ray and other high energy radiations are counted. Since the maximum energy of the tritium betas is 18 kev, 575 divisions = 18 kev and the operating discriminator setting (e.g. 60 divisions) = 1.88 kev by direct proportionality. Thus during the measurement, only tritium betas with an energy greater than 1.88 kev were actually counted. From

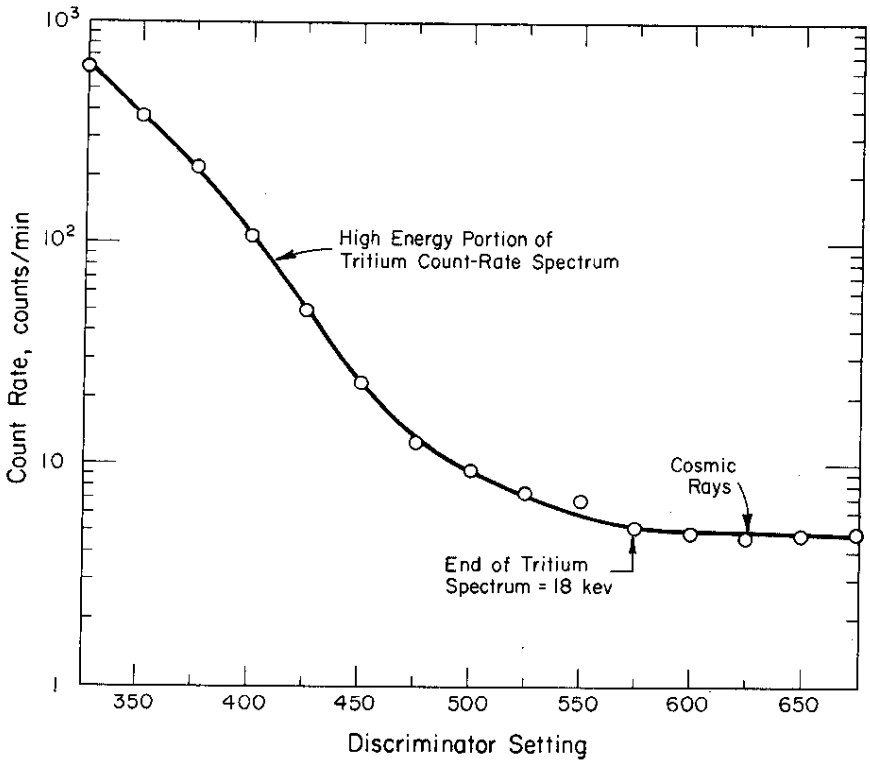

FIG. 8 TRITIUM END POINT CURVE

a plot of the number of tritium betas per energy interval vs. beta energy[8] (Figure 9), it is possible to determine what fraction of the betas were counted. A calibration plot is given in Figure 10. Thus for a given operating discriminator setting and a measured end-point discriminator setting, the counting efficiency, i.e. fraction of betas counted, can be determined. In the example given, the counting efficiency is 80%.

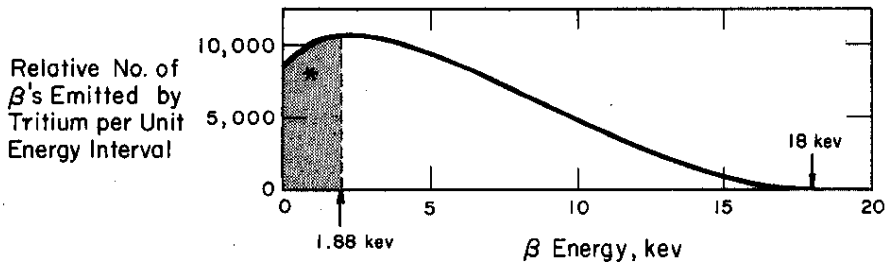

FIG. 9 NUMBER OF T BETAS WITH ENERGY E AS A FUNCTION OF ENERGY
(*Shaded area represents fraction of T betas that are not counted)

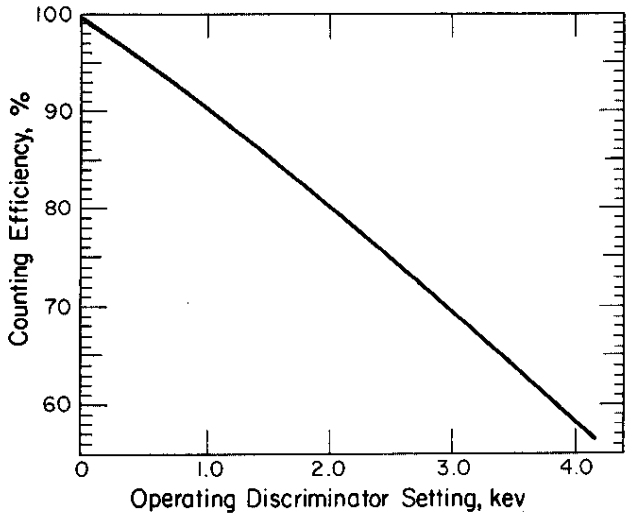

FIG. 10 CALIBRATION PLOT - COUNTING EFFICIENCY vs DISCRIMINATOR SETTING

Since all of the tritium in the system is not in the proportional counter, a correction must be made for this factor.

Therefore the system efficiency is:

$$\frac{\text{Counts}}{\text{Beta disintegration}} = \frac{\text{Volume of proportional counter}}{\text{Volume of total system}} \times \text{counting efficiency}$$

OPERATING DETAILS

The following comments on operating details are provided for the benefit of those who have not previously employed this type of measuring equipment.

First, the count rate of a given proportional counter is a function of the P-10 gas pressure as shown in Figure 11. To minimize changes in count rate resulting from small pressure fluctuations, it is desirable to avoid operation at P-10 pressures that are on the steeper portion of this typical curve - 54 cm of Hg is satisfactory.

Experience shows that the residual tritium contamination present in the system, after a measurement, can best be removed by a combination of alternating evacuations and flushes with P-10 gas. This process can be speeded up with the judicious application of heat to the system piping.

The high voltage employed with this system (1750 volts) provides a gas amplification in the proportional counter of approximately 200.

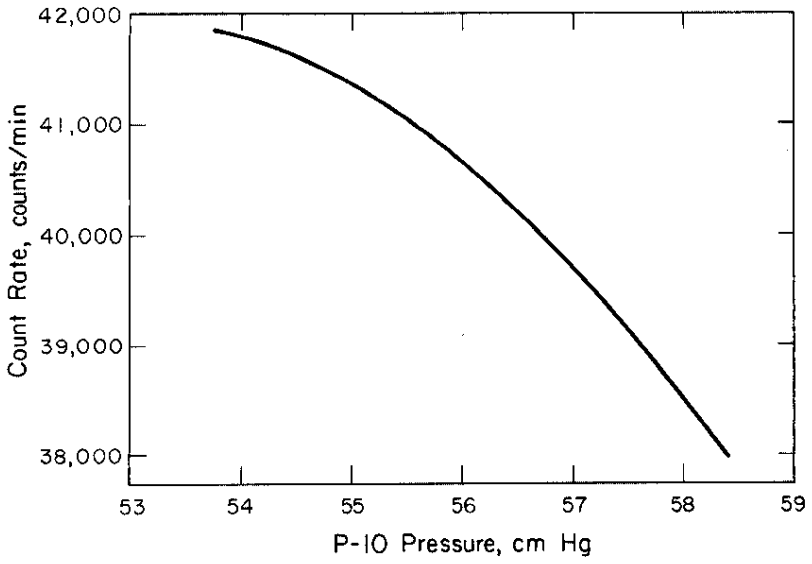

FIG. 11 COUNT RATE vs P-10 PRESSURE

ACKNOWLEDGMENT

L. Cathey, M. H. Goosey, H. W. Randolph, R. H. Searle, and L. G. Stone contributed significantly to the specification and fabrication of the equipment described.

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