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Radon Fluoride; Further Tracer Experiments With Radon, ~~(1)~~

MASTER

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CONF-126-10

Abstract

It has been shown in tracer experiments that radon fluoride can be prepared by heating mixtures of radon and fluorine to 400°C. The compound is very stable and distills at 230 to 250° at a pressure of approximately 10^{-6} mm Hg. It can be reduced with hydrogen at 500° to recover elemental radon.

Attempts to prepare a radon chloride by thermal and photochemical methods have been unsuccessful thus far. No chemical reactions have been detected in mixtures of radon and oxygen irradiated with ultra-violet light or passed through a Berthelot type ozone generator. However, it has been observed that the high-voltage electrical discharge used to produce ozone causes some radon to be strongly fixed on Pyrex surfaces. Microwave discharges have also been found to be very effective in fixing radon on quartz and Pyrex. In experiments with a metal microwave cell, radon has been fixed on a central brass antenna and subsequently released by heating the brass to the softening point (~ 900°).

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DISCLAIMER

After the existence of fluorine compounds of xenon had been clearly demonstrated by Bartlett (2) and Claassen, Selig, and Malm (3), it was shown in tracer experiments (4) that radon also forms a stable compound with fluorine. Radon fluoride was first prepared in a metal vacuum line of the type shown in Figure 1. Gaseous radon-222, obtained from 2 mg of radium chloride in aqueous solution, was passed through a magnesium perchlorate drying tube into a 100 cc Pyrex bulb. The bulb was then attached to the prefluorinated nickel and Monel vacuum line, and part of the radon was condensed in trap B at -195°. When the trap was warmed to -78°, it was demonstrated that the radon moved readily under vacuum into other parts of the line which were cooled to -195°. Since radon decays by emission of alpha particles, which cannot penetrate heavy-walled vessels, the radon position was determined by counting the 1.8 MeV gamma activity of a subsequent daughter, Bi^{214}. The radioactive decay scheme, from Ra^{226} to Pb^{206}, is shown in Figure 2. The Bi^{214} grew into equilibrium with radon wherever the latter appeared and decayed where it disappeared, within several hours. The gamma counting was done with sodium iodide scintillation detectors, shielded by lead bricks, and a 400-channel pulse-height analyzer.

Radon fluoride was prepared in several experiments by condensing 5 to 100 microcuries of radon in a 5 cc nickel reaction vessel at -195°, adding fluorine to 300 mm pressure, and heating the mixture to 400° for 30 minutes. When the vessel was cooled to -78° and the excess fluorine was pumped off, it was found that the radon remained fixed in the reaction vessel. The compound which had been formed did not distill in a vacuum of 10^{-5} to 10^{-6} mm until heated to a temperature of 230° or higher. In some instances, a reaction vessel with a capillary inlet tube was used, and the compound could then be concentrated in a small section of the metal capillary by distillation at 230 to 250°. In one experiment, a mixture of xenon and radon was fluorinated; the xenon fluoride product was distilled at 50° into a cold trap at -195°, leaving the less volatile radon fluoride behind.

Radon fluoride can be reduced with hydrogen at 500° to recover elemental radon. At 200° the compound does not appear to react with hydrogen. The composition of the compound has not yet been determined, but attempts are being made to vaporize samples inside a time-of-flight mass spectrometer for stoichiometric analysis. The tracer quantities of radon fluoride prepared thus far have shown no evidence of radiation decomposition from alpha particle emission. However, the compound has been present in very dilute form on the inner surfaces of the container vessels, and most of the energy of the alpha particles has therefore been absorbed by the metal walls rather than by the compound.

Attempts have recently been made to prepare other radon compounds by thermal, photochemical, and electrical discharge methods, using 2 to 260 microcurie amounts of radon and milligram or gram amounts of other chemicals. Whereas elemental radon distills in vacuum from a cold trap at -78°, it is assumed that radon compounds in general will not distill at this temperature. Reduction in volatility of the radon has therefore been used as a simple criterion for compound formation, although it is recognized that very volatile compounds may not be detected by this method. In the first attempt to prepare a radon chloride, 16 microcuries of radon was mixed with chlorine at 150 mm pressure in a quartz U-tube, and the mixture was heated to 400° for 45 minutes. The U-tube was cooled to -195° to condense all the radon and chlorine, then warmed to -78°; at this temperature both the radon and chlorine distilled into a cold trap at -195°, indicating that no compound of low volatility was formed. When the same mixture was heated to 800° for 90 minutes and rapidly quenched in liquid nitrogen, similar results were obtained. A mixture of 2.8 microcuries of radon and approximately 0.3 ml of iodine monochloride, heated to 500° for 20 minutes, also gave no evidence of reaction. The effect of ultra-violet light on 9.8 microcuries of radon and chlorine at approximately 150 mm pressure was studied in a quartz cell of 4-inch path length. The mixture was irradiated with light from a high-pressure mercury arc for 64 hours, with the gas circulated through the cell by a convection loop operating between 0° and 80°. Again no compound appeared to be formed.

The effect of ozone on radon was first studied photochemically. The quartz cell was filled with 18 microcuries of radon and oxygen at 165 mm pressure, then irradiated for 40 hours at room temperature with intense light, predominantly of 2537 Å wavelength. Although a small amount of ozone was produced, no evidence of reaction with radon was obtained. The effect of higher concentrations of ozone was then studied with the apparatus shown in Figure 3. Ozone was generated by circulating oxygen at 50 to 500 mm pressure through a Pyrex Berthelot tube (5), which was immersed in dilute copper sulfate solution with the electrodes connected to a 15,000 volt transformer. In some instances a heating tape was used above the cold trap to produce gas convection through the ozone generator; in others, liquid oxygen was condensed in the supply bulb and distilled slowly through the generator to the cold trap. A mixture of ozone and oxygen was collected in the trap at

-195°, and most of the oxygen was then pumped off, leaving the less volatile ozone in the trap. With Halocarbon grease on the stopcocks, the ozone decomposed very slowly, even at room temperature. Several experiments were tried in which radon was mixed with the oxygen beforehand and circulated through the ozonizer to the cold trap, which was either at -195° or -78°. The radon in the trap appeared to be unchanged, since it remained volatile at -78°. In other experiments, radon was frozen initially in the trap at -195°, ozone was then generated and collected in the trap, and the mixture was allowed to warm to room temperature overnight. Again no evidence of compound formation was obtained.

It was observed, however, that whenever radon-oxygen mixtures were circulated through the ozone generator, approximately 5 to 20% of the radon was fixed inside the generator within several hours. The tracer radon was bound to the glass of the Berthelot tube very strongly and could not be removed by vacuum distillation at 450° or by heating the tube with hydrogen at 500°. When the ozone generator was cut from the line and the inside was washed with cold distilled water, 2 molar nitric acid, and 6 molar nitric acid, very little of the fixed radioactivity was removed. Hot 6 molar nitric acid removed approximately 50 percent of the radon daughters, with little effect on the fixed radon, since the gamma activity grew back within several hours. Cold 6 molar sodium hydroxide removed both radon and daughters, probably by dissolving a thin layer of the glass.

The effect of microwave discharges was investigated with the apparatus shown in Figure 4. Approximately 260 microcuries of radon was first condensed in a small quartz bulb, oxygen was added to 5 mm pressure, and the bulb was placed near the director of a Raytheon Model CMD4 diathermy unit, which generates microwaves of 12.3 cm wavelength. A discharge was started with a Tesla coil and allowed to continue for 145 minutes. When the oxygen was pumped out at -78°, all of the radon remained in the bulb. It was found to be distributed over the bottom half of the bulb in the region where the glow discharge had occurred. When the bottom section was strongly heated in vacuum, the radon daughters distilled out of the bottom at approximately 600° and condensed in a ring on the cooler upper section. It was clear that the radon did not move, however; the gamma activity of the ring decayed when the system was left overnight at room temperature, and the activity grew back into the bottom section. The process was repeated at a temperature of 970° with similar results. The radon deposit was also heated with hydrogen at 970°, but very little radon was removed by this process.

Since the tracer quantity of radon had a negligible partial pressure in each experiment, it was necessary to add another gas to produce an ionizing discharge. The radon was fixed when the diluent gas was oxygen, nitrogen, or helium at about 5 mm pressure. Quartz bulbs were generally used, but the results were the same when Pyrex bulbs were substituted. With discharges of 30 to 145 minutes duration, the percentage of radon fixed varied from 10 to 100 percent in different experiments. The effectiveness of water and solutions of nitric acid and sodium hydroxide in washing off the activity was the same as described for the ozone generator.

The microwave cell shown in Figure 5 was devised so that discharges could be produced in a metal system. A 3/4-inch O.D. nickel test tube was attached by a standard tapered joint to a brass chamber, which was connected to the vacuum line by a side-arm. Another side-arm, fitted with an insulated vacuum seal, transmitted energy from the microwave generator to a threaded brass rod, which served as an internal antenna. A mixture of radon and another gas could be added to the cell at low pressure, and a discharge could be produced in the region between the bottom of the brass rod and the nickel test tube. A Pyrex window at the top of the cell was used to watch the discharge, and the system was tuned by adjusting the position of the rod, which was approximately two wavelengths long. It was found that the efficiency was low, since the ionization was produced in only a small fraction of the total volume. In one experiment, a 30 minute discharge with 23 microcuries of radon and oxygen at approximately 2 mm pressure fixed 25 percent of the radon. In a second trial, no radon was fixed, apparently as the result of too high a pressure of oxygen (> 10 mm). Other results were: 42 microcuries of radon and 4 mm oxygen pressure, 22 percent fixed in one hour; 122 microcuries of radon and 2 mm oxygen pressure, 37 percent fixed in one hour.

Almost all of the fixed radon appeared on the bottom of the brass antenna rod; very little was found on the walls of the nickel test tube. The voltage gradients produced by the microwave field apparently caused radon ions to be preferentially driven into the antenna. The bound radon was present in a thin surface layer, since it could be removed by etching the brass with 6 molar nitric acid. At the conclusion of the experiments with this apparatus, the bottom section of the brass antenna with a radon deposit was cut into small pieces and gradually heated in vacuum. At approximately 900°, near the softening point of the brass, the radon escaped and moved to a cold trap on the vacuum line.

From the foregoing experiments it can be concluded that only the reaction of radon and fluorine yielded a definite compound in the present investigation. Chlorine, iodine monochloride, oxygen, and ozone gave no evidence of reaction with radon under the conditions which were used. The results obtained with high-voltage and microwave discharges can probably be attributed to physical processes involving ion bombardment of the walls, since similar results with other isotopes have been reported by previous investigators.(6-9) However, the possibility of chemical stabilization of the radon by formation of an oxide or silicate cannot be entirely discounted. The stability of radon imbedded in quartz is quite remarkable, considering that radon daughters such as Bi^{214} or its precursors, Po^{218} and Pb^{214}, can be removed at 600°, leaving the radon firmly bound. No doubt practical applications of the electrical discharge methods can be found, such as the preparation of radon sources for medical and other purposes.

References

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Fig. 1. Vacuum line for the preparation of radon fluoride.

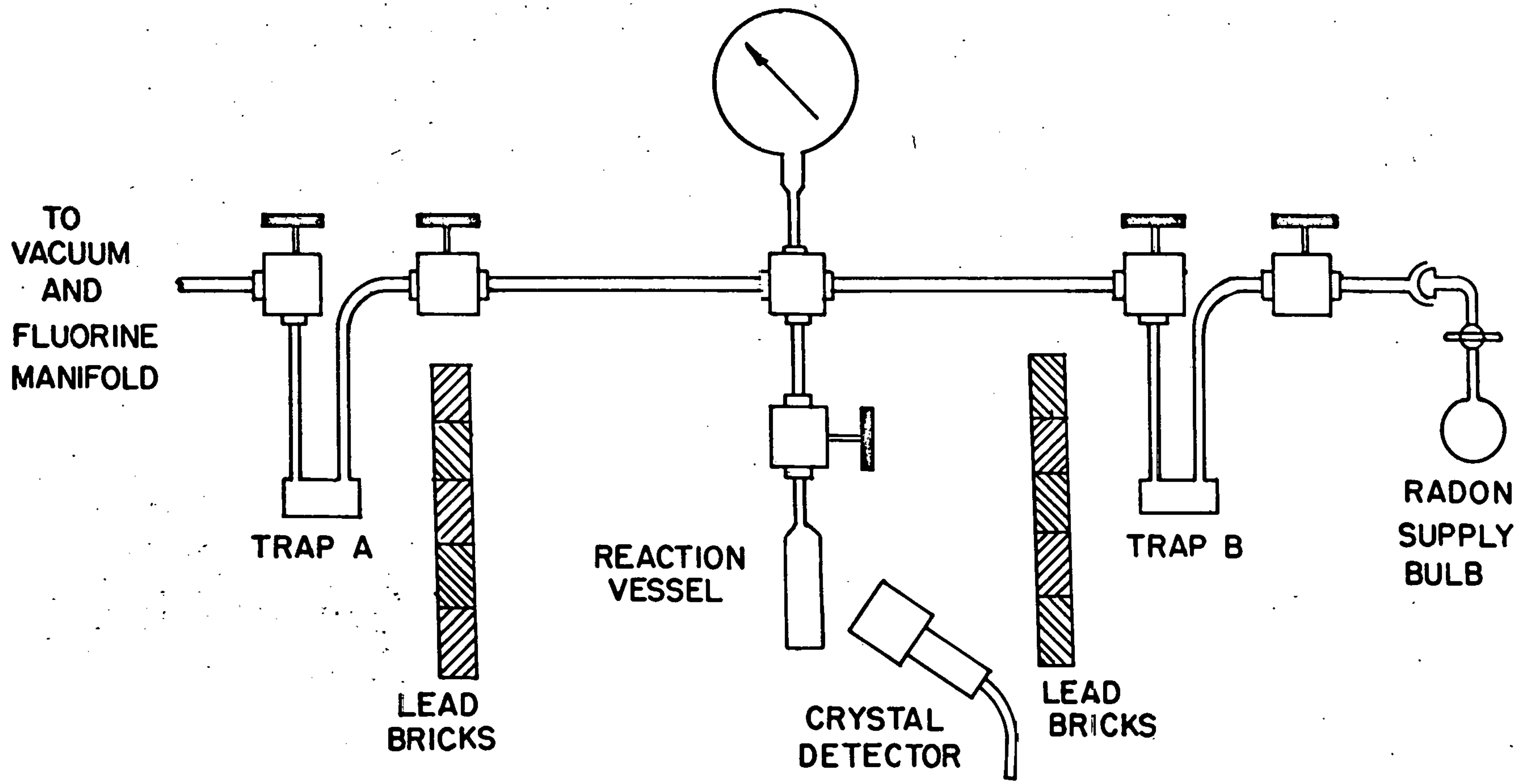
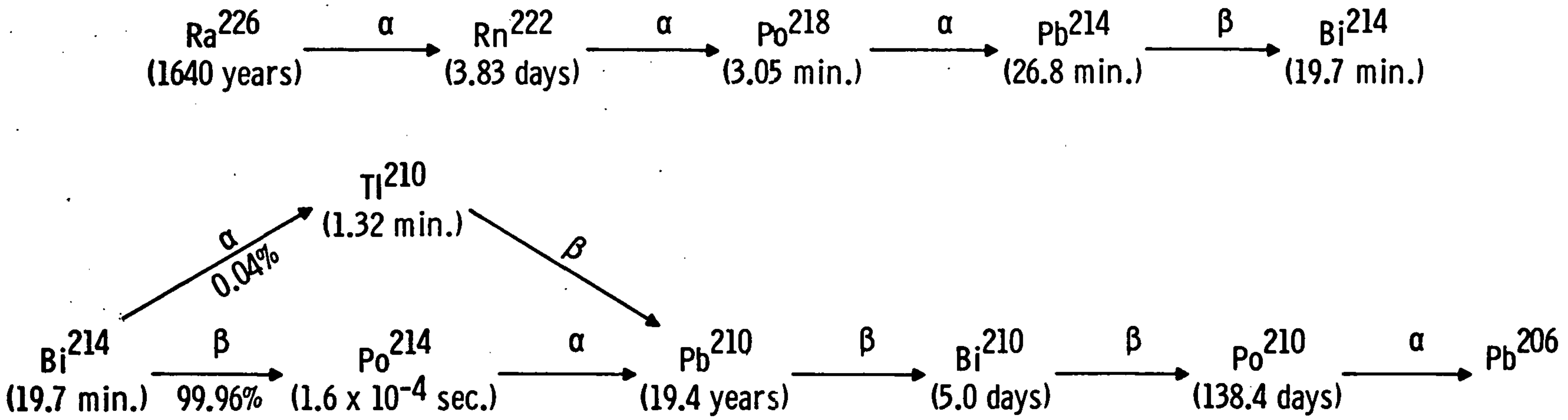
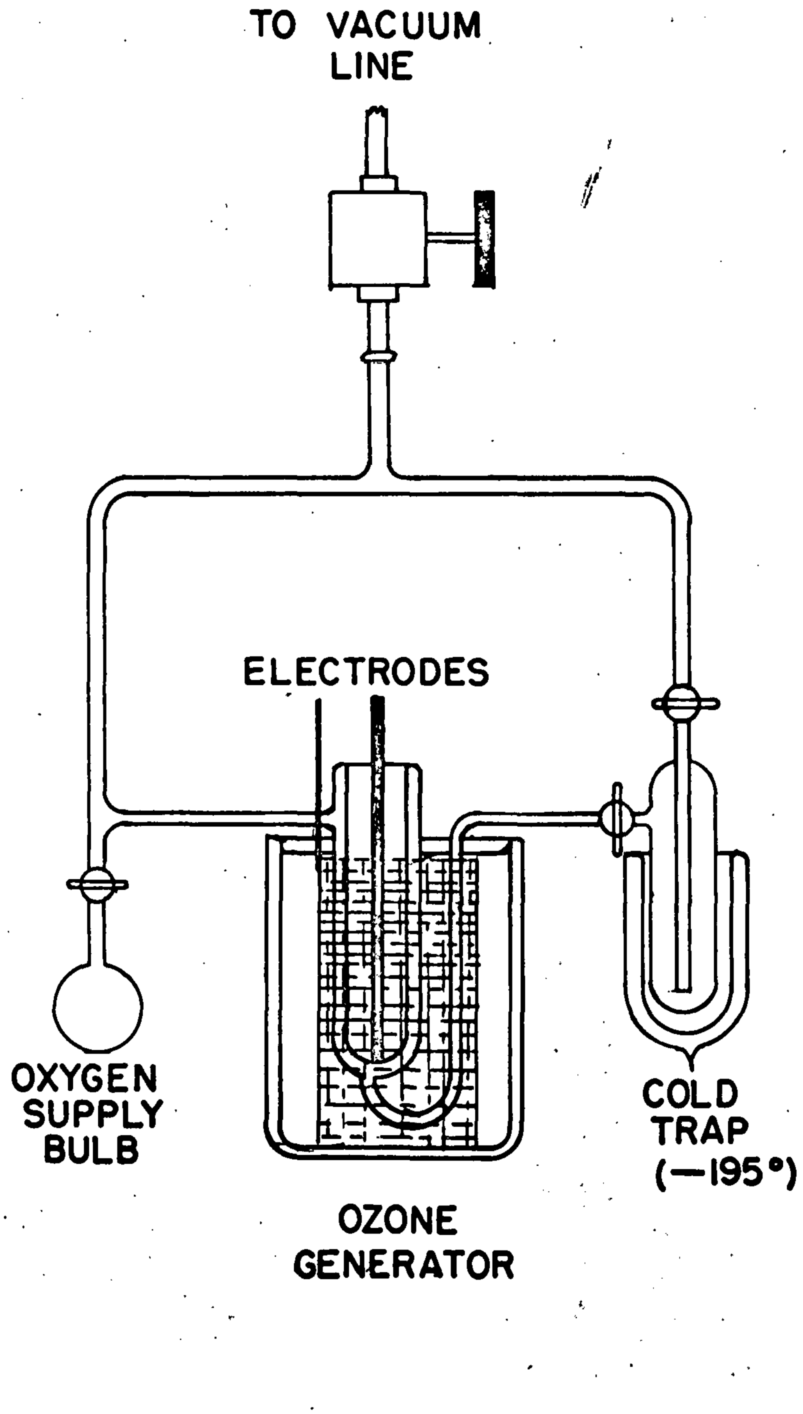

TO VACUUM AND FLUORINE MANIFOLD
TRAP A
LEAD BRICKS
REACTION VESSEL
CRYSTAL DETECTOR
LEAD BRICKS
TRAP B
RADON SUPPLY BULB

Fig. 2. Radioactive decay of Ra^{226} and subsequent daughters.



Ra226
(1640 years)
α
Rn222
(3.83 days)
α
Po218
(3.05 min.)
α
Pb214
(26.8 min.)
β
Bi214
(19.7 min.)
Tl210
(1.32 min.)
α
0.04%
β
Bi214
(19.7 min.)
β
99.96%
Po214
(1.6 x 10-4 sec.)
α
Pb210
(19.4 years)
β
Bi210
(5.0 days)
β
Po210
(138.4 days)
α
Pb206

Fig. 3. Apparatus for experiments with ozone and radon.



TO VACUUM LINE
ELECTRODES
OXYGEN SUPPLY BULB
COLD TRAP (—195°)
OZONE GENERATOR

Fig. 4. Apparatus for producing microwave discharges in quartz.

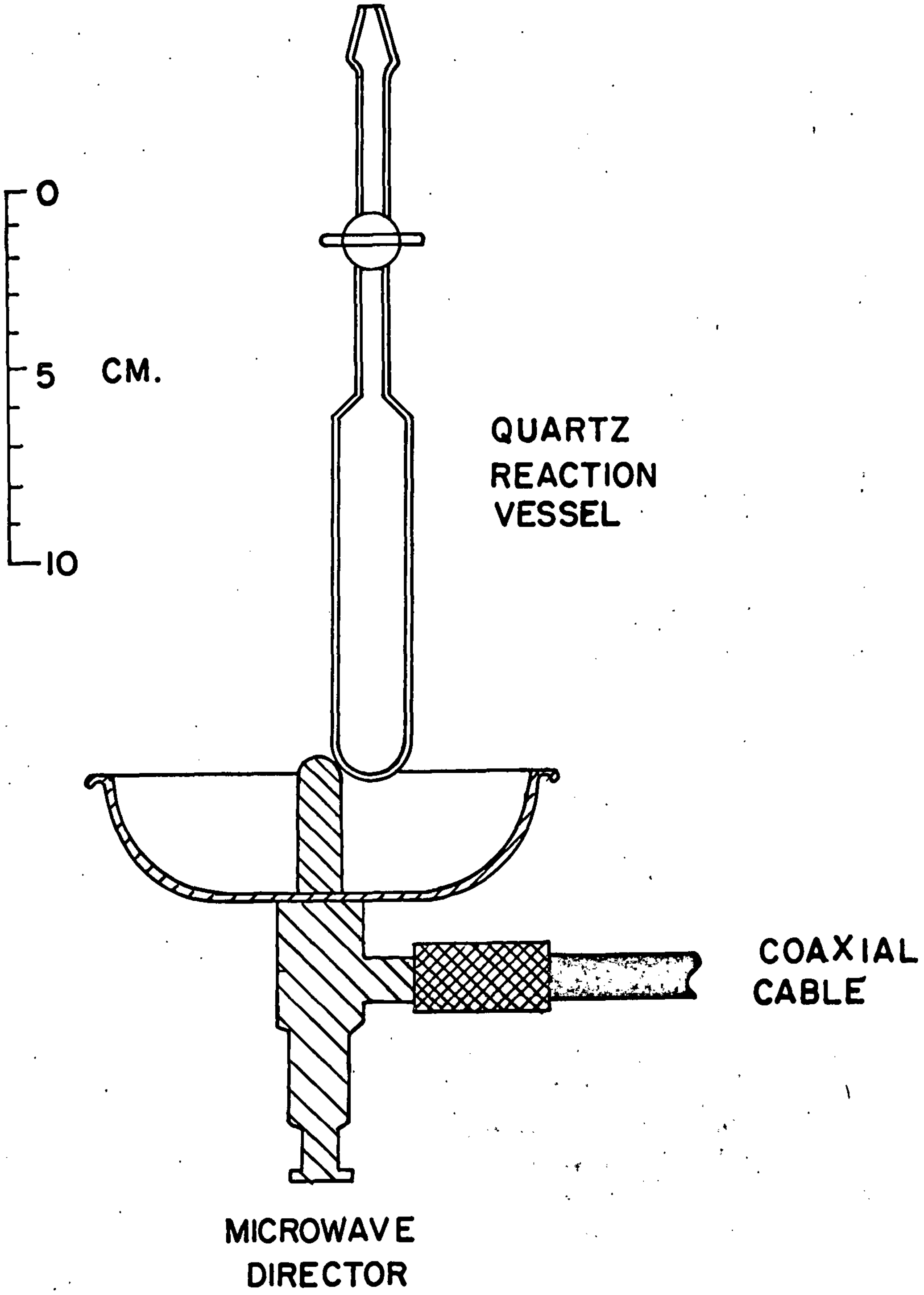
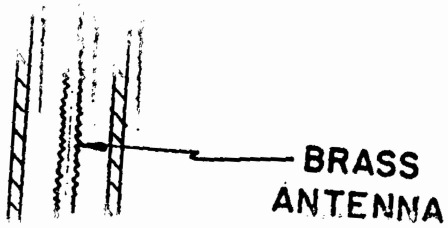
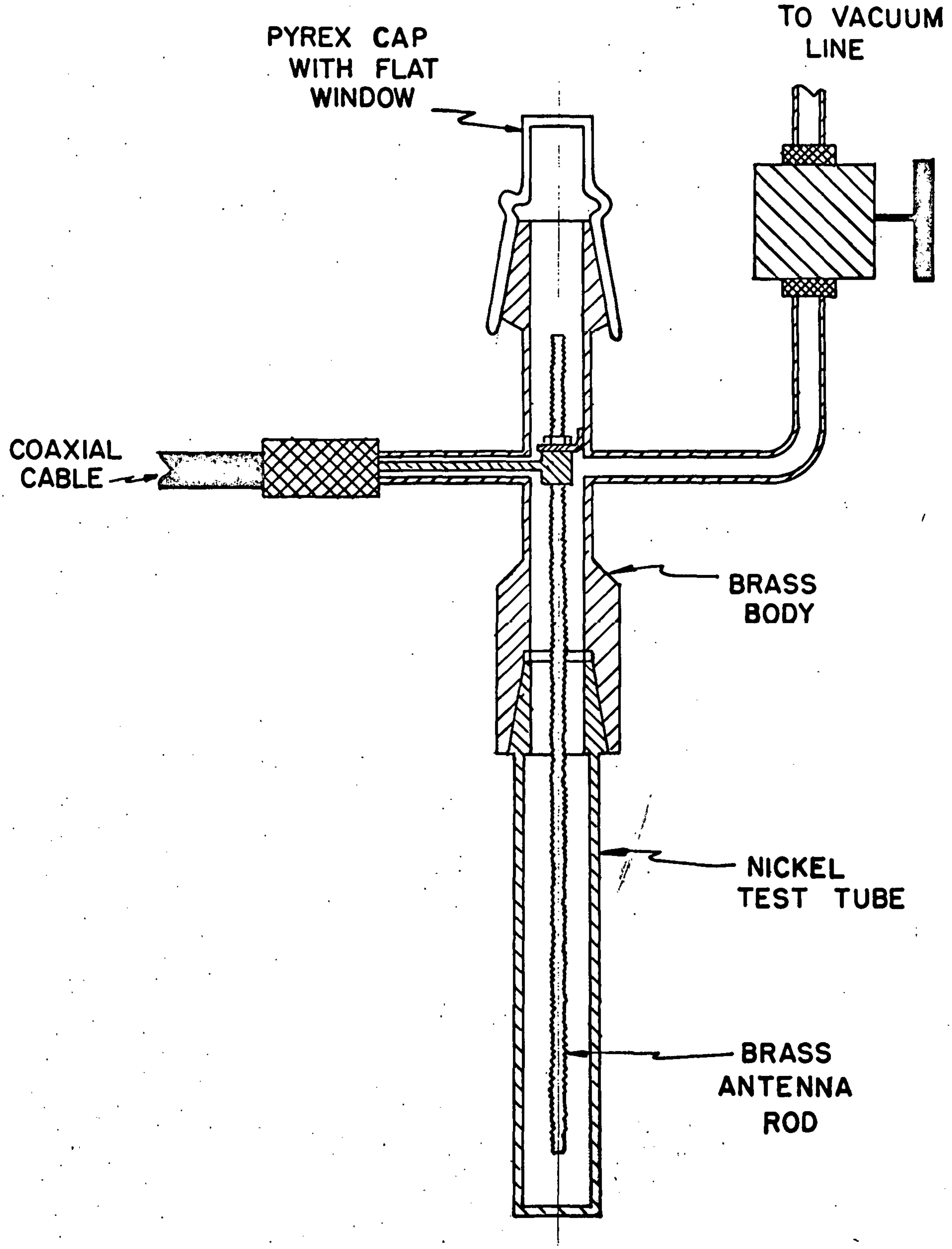

0
5
CM.
10
QUARTZ REACTION VESSEL
COAXIAL CABLE
MICROWAVE DIRECTOR

Fig. 5. Metal microwave cell.




PYREX CAP
WITH FLAT
WINDOW
TO VACUUM
LINE
COAXIAL
CABLE
BRASS
BODY
NICKEL
TEST TUBE
BRASS
ANTENNA
ROD