New Precision Technique for Removing Radioactive Emanations from Matter, and for Measuring Minute Quantities of Radon and Thoron

Thesis by

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LIST OF ILLUSTRATIONS

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ABSTRACT

I INTRODUCTION

The accurate determination of the radium content of ordinary matter has many applications in cosmology and geophysics, but is a difficult analysis to carry out. Two problems are involved, first the removal of radon from the material being tested, then the accurate measurement of this radon by means of its alpha ray ionization. The radon removed and measured is about 10^{-18} gm.

II REMOVAL OF RADON FROM MATTER

The principles used heretofore for removing radon from liquids are modified somewhat, and the apparatus given a simplified and entirely new form. The estimated uncertainty of measurement is now less than 1%.

A new principle for removing radon from rocks, involving an entirely different and much simpler type of apparatus is presented. Powdered rock specimens are boiled without flux by direct heating to 1800°C in a vacuum, graphite resistance furnace. The gases are led to the ionization chamber through a simple electrostatic ion-trap which removes all the ionized molecules coming from the boiling granite. All moisture absorbents and reservoirs are eliminated from the gas line, a small insulation drying device in the ionization chamber protecting the amber insulation from deleterious vapors.

A systematic study of the percentage of the total radon removed as a function of (a) temperature, (b) time of heating, and (c) fineness of sample grains, showed that temperature is the only important factor and that 1800° effects complete radon removal. The duration of heating

is 2 1/2 min., which is to be compared with one hour for the quickest of former methods.

III MEASUREMENT OF SMALL QUANTITIES OF RADON

In the measurement of small quantities of radon, emphasis is laid on accurate knowledge of the background ionization due to cosmic and local radiation. The statistical variations in the background are shown to impose the natural observation limit in these measurements, and twenty possible sources of background are discussed with a view to minimizing these variations.

A new bifilar, vacuum,removable-head electrometer with multiple ionization chambers is described. The ionization chambers contain a small insulation drying room, thus permitting the use of moist gases.

The absolute or radium calibrations of the electrometer-ionization-chamber system by two radium standards and by the empirical formula of Duane and Laborde are critically discussed.

A new theoretical formula for the wall effect with alpha particl and for the radium calibration of emanation electrometers,in terms of their easily measured physical properties,is presented and shown to agre with the experimental calibrations involving radium standards.

The limit of precision of the bifilar electrometer is shown, and a new apparatus described which will extend the measurements to the natural observation limit. The nub of this apparatus is a sensitive string electrometer which measures only the difference in ionization in two identical ionization chambers both of which contain the same background gases, but only one of which contains the radon or thoron to be measured.

IV. DETERMINATION OF THORIUM

It is shown that the thorium as well as the radium content of matter can be determined in a single run. Like radon, thoron is removed from rocks by direct heating, the threshold temperature being 850°C for biotite granite. The determination of the temperature of complete removal and the absolute calibration of the electrometer in terms of thorium await the completion of an all-metal gas circulating pump, the design of which is briefly described.

V. BY-PRODUCTS OF THE INVESTIGATION

Three appendices discuss the construction and characteristics of three other furnaces developed in the course of the investigation. The vertical, split-tube, graphite resistance furnace described is particula ly suited to a variety of chemical and mineralogical investigations. It maintains 2000°C on only 7 kilowatts of power input.

The first artificial production of cristobalite is tentatively asserted; micro-chemical confirmation analyses being in progress.

INTRODUCTION

A reliable method for measuring the radioactive content of ordinary terrestrial rocks, waters and deposits is important in the solution of several problems in cosmology and in geophysics. Foremost among these problems are the ages of the solar and extra-solar systems, which are determined by radioactive analysis of meteorites; the problem of terrestrial heat, involving the unbelievably low concentration of radioactive material at the earth's center; the correction of cosmic ray readings for local radiation; the location of fault lines; and the correlation of geological strata, particularly those of Precambrian age.

The radium content of ores can be measured[1] by the intensity of the gamma rays emitted from them if the radium content exceeds 2×10^{-9} gm. radium per gm. rock, but the gamma ray method finds its principal application in the measurement of material containing more than 10^{-7} gm. radium per gm.

More sensitive methods utilize the great ionization produced by alpha particles. Radon, the gaseous, inert, first decay product of radium is separated from the material to be analyzed, and the ionization produced by the alpha rays of the radon and its solid decay products is measured. This gives the quantity of radon associated with the radium in the material tested, from which the radium content can be easily calculated. Similarly, the thorium content can be measured by releasing and measuring the thoron.

Measurements of the radioactive content of solids or liquids of low activity thus involve two distinct problems, first the complete re-

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[1] Hess, Am. Electrochem. Soc. Trans., 41, 287, (1922).

moval of the radioactive emanations from the sample, then the accurate measurement of the emanation removed. These problems are separately treated below.

This thesis presents new solutions to both of these problems, and describes the present status of a search for satisfactory, simple methods of analysis, together with a thorough knowledge of their limitations and applicabilities. The course of the investigation is interrupted only for the preparation of the following pages, which contain a record not only of the work accomplished but brief suggestions of the work projected.

I REMOVAL OF RADON FROM MATTER

A RELEASE OF RADON FROM LIQUIDS

The solubility of radon in water1) and other solvents2) obeys Henry's law, on which all methods of freeing radon from liquids are based.

Radon can be removed from solutions by bubbling a radon free gas (air, CO_2) through the solution at room temperature. This method is generally regarded as unreliable3). Moran4) has demonstrated that bubbling must be continued for about 3 hours before a reproducible condition is realized, and even then the release of radon is incomplete and strongly dependent on the temperature.

Radon can be removed by simply boiling the solution containing it. Particularly when the volume of the solution is small compared with the volume of the system receiving the radon, this method is successful, since the boiling produces violent agitation, hastening equilibrium, while the elevated temperature reduces r, the relative volumetric concentration of radon between the liquid and gaseous phases, to 0.107.

The aspirating and boiling methods can, of course, be used simultaneously5). Other techniques include the shaking method6) for field work, wherein agitation for equilibrium is obtained by mechanical shaking but atmospheric temperature is used. (At $0^\circ C$, $r = 0.510$; at 20°,

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1) For literature see St. Meyer and E. Schweidler, Radioaktivitat, (192
p. 411.

2) loc. cit. p. 412.

3) Rutherford, Chadwick and Ellis, "Radiations from Radioactive Substance
Macmillan 1930, p. 567.

4) Moran, Trans. Roy. Soc. Canada, 10, III, 57, (1916); 10, III, 77, (19

5) Bothe, Zeit. f. Ph., 16, 266, 1923.
Paneth and Koeck, Zeit. f. Phy. Ch. Bodenstein Festband, p. 145, 1931

6) Schmidt, Phys. Zeit., 6, 561, (1905).
Hootman and Nelms, Am. Jour. Sci., 21, 37, (1931).
Hootman, Am. Jour. Sci., 22, 453, (1931).
Ramsey, Am. Jour. Sci., 40, 309, (1915).

r = .255).

Formerly the apparatus used for the boiling method has been complicated by a gas burette[1] containing NaOH solution to absorb CO_2 emitted from the solution. Naturally the NaOH solution itself absorbs radon. McMillan, in some unpublished experiments with a similar NaOH tube[2] found as much as 17% of the radon present was held up in this solution, even when it was carefully boiled after passing the radon bearing gas through it. In his experiments a small ionization chamber of about 600 cc. volume was used. The discussion on p. 72 indicates that this NaOH solution is a needless precaution even when air is used for filling the ionization chambers, and its usefulness vanishes completely when CO_2 is used in the chambers.

The usual apparatus has been completely modified in the present work. In Fig. 1, p. 12, F is the flask in which the sample to be tested has been sealed up by means of the shellaced rubber stopper and the fine tips drawn on the glass tubes T_1 and T_2. When the measurements are to be made the flask is connected to the apparatus, now containing CO_2 at about 400 mm Hg pressure by heavy rubber tubing collars, C, and then the tips of the tubes T_1 and T_2 are crushed with pliers.

The internal electric heater, H, consisting of 3 feet of 30 gauge chromel "A" wire wound on T_1, is now supplied with 5 amperes from a 110 volt A.C. source and the solution vigorously boiled for 20 minutes to assure complete radon removal. The vapors from the boiling solution pass upward into the bulbous reflux condenser, R, where the water vapor

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1) Lind, U.S. Bureau of Mines Bulletin 212, (1923), p. 194.
Bohn, Ph.D. Thesis C.I.T. (1928).
2) Mc Millan, M.S. Thesis, C.I.T. (1929).

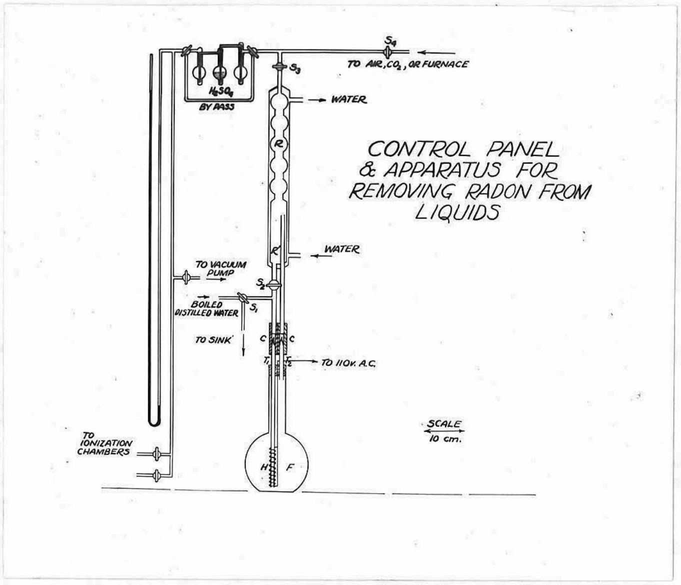

Fig. 1. Apparatus for removing radon from liquids.

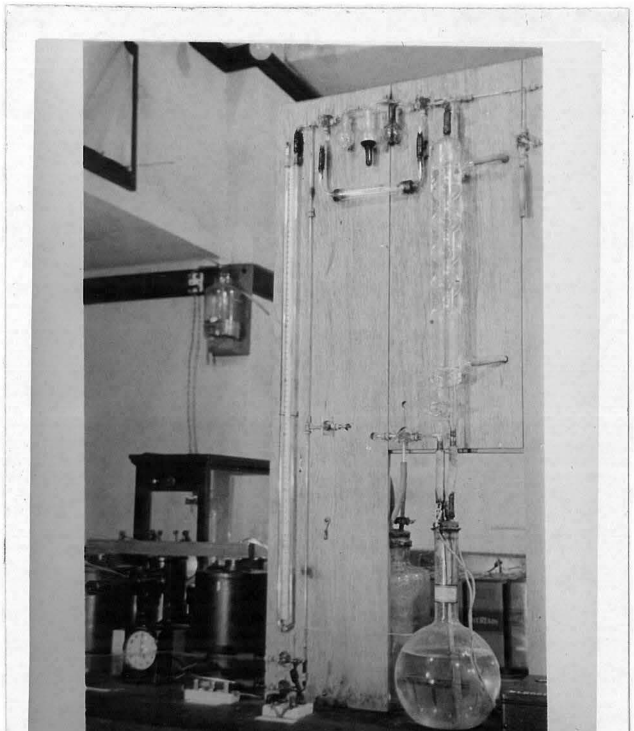

Fig. 2. Control panel and apparatus for removing radon from liquids. The overhead boiler (p. 13) is seen in the left background; the ionization chambers in the left foreground.

is condensed and returned to the reservoir, R', thence back to the bottom of the boiling solution through T_1, thus contributing to the agitation of the solution and completely relieving the reflux condenser of the carry-over difficulties prevalent in ordinary single tube reflux condensers.

The radon and other gases, O_2, CO_2, etc., liberated from the solution then pass through a sulfuric acid micro-cell, flanked by protective traps, and on to the ionization chamber. This cell, while perfo ing some drying function, is far more important as a one way valve for t radon. Through its valvular action the volumetric concentration of rado can be built up in the ionization chamber, while being reduced to a very low value over the boiling solution, and hence to a negligible value in the solution, since $r = 0.107$.

Moisture passing the sulfuric acid cell and entering the ionization chamber has no observable effect on the insulation because of the special drying-room surrounding the amber, which is described fully on p. 50.

After the conclusion of the boiling, S_2 is closed and the space in the flask above the liquid, as well as the reflux condenser, is completely filled with hot, distilled water through the stopcock S_1 from an overhead boiler, equipped with an internal heater similar to H. This forces any radon remaining in the gas space above the solution through the acid valve into the ionization chamber. Because the distilled water enters the flask through T_1 below the liquid surface there is no agitation of the upper surface and hence negligible reabsorption of radon at the rising hot water surface.

The stopcock S_3 is then closed and the ionization chamber brought up to pressure with CO_2 introduced through stopcock S_4. This gas bubble through the sulfuric acid cell, reducing the small quantity of radon which it has absorbed to a wholly negligible value[1,2].

Ordinary well waters and tap water contain the order of 5×10^{-10} curie of radon per liter. The radon from 1 cc. of such water could be detected by the bifilar electrometer described on p.47, but ordinarily 2 liter samples are run. It is clear that the activity can therefore be measured to about 0.1%, and with the apparatus as described above successive samples from the same source (well, etc.) vary from one another by less than 1%. These may very well be actual variations in the samples.

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1) Eve and McIntosh, Phil. Mag., August 1907.
2) Ebler and van Rhyn, Ber. deutsch. Chem. Ges., 54, B p. 2896, (1921); 44, 2332, (1921); Zeit. Anorg. Chem., 73, 1, (1911).

B. RELEASE OF RADON FROM SOLIDS

There have been two general methods for the removal of radon from rocks. The present research developed a third method, which possesses marked advantages over the earlier methods.

1. THE CARBONATE FUSION METHOD

Many observers[1-10] have used the carbonate fusion method introduced by Joly[1], in which a few grams of powdered rock are mixed with sodium and potassium carbonate, and the mixture fused in a furnace. It is claimed that the flux dissolves the rock, releasing its radon content at a moderate temperature, usually below 1000°C. Heating is usually continued for about an hour, but no one has carried out a systematic investigation of the effects of time and temperature on the relative completeness of radon removal. Buchner[11], and Lind and Whittemore[12] have presented general objections to the carbonate fusion method, while others[13] have particularly criticized Joly's technique.

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[1] Joly, Phil. Mag., 17, 760, (1909); 18, 140, (1909); 22, 134, (1911); 24, 694, (1912).

[2] Joly and Poole, Phil. Mag., 48, 819, (1924); 3, 1233, (1927).

[3] Poole, Phil. Mag., 40, 466, (1920); 3, 1246, (1927).

[4] Piggot, Am. Jour. Sci., 17, 15, (1929); 21, 28, (1931).

[5] Piggot and Merwin, Am. Jour. Sci., 23, 49, (1932).

[6] Strutt, Proc. Roy. Soc., A, 77, 480, (1916).

[7] Quirke and Finkelstein, Am. Jour. Sci., 44, 237, (1917).

[8] Behounek and Santholzer, Gerl. Beitrage z. Geophysik, Koppen Band II (1931), p. 60-69.

[9] Bohn: Ph.D. Thesis, C.I.T. 1928.

[10] Mc Millan: M.S. Thesis, C.I.T. 1929.

[11] Buchner, Jahrbuch d. Rad. u. Elektr., 10, 516, (1913).

[12] Lind and Whittemore, U.S. Bureau of Mines, Tech. Paper 88, (1915), p
Jour. Am. Chem. Soc., 36, 2066, (1914).

[13] see ref. 4), 8), 9), 10) above.

In general, the carbonate fusion method never has been clearly demonstrated to secure complete removal of radon, while Lind and Whittemore have definitely shown their own carbonate fusion technique to be a failure for carnotite ores, probably because of insufficient temperature. For the treatment of pitchblend and crude sulfates the method is generally accepted.

2. THE SOLUTION METHOD

The solution method involves dissolving the rock completely in an acqueous, acidic solution, and removing the radon from this solution by the method for water samples described on p. 10. Lind and Whittemore have obtained consistent determinations of carnotite ores by dissolving the sample in 1:1 HNO_3, leaving the silica undissolved. This method might be applicable to some ordinary rocks but it could not safely be used indiscriminately. All other experimenters attempt to obtain a clear solution, with the silicates dissolved, but it is well known that even if the vicissitudes of dissolving the rock are surmounted the solution is difficult to keep clear. Colloidal silica precipitates out and adsorbs the radon1), holding it in the solution against efforts to remove it by boiling or aspiration.

The common prelude to the solution method is a carbonate fusion to dissolve the silica, the melt is then dissolved in 5 per cent Na_2CO_3, filtered, and the residue dissolved in 1:3 HNO_3 solution. Even in these solutions enough colloidal silica almost invariably forms to make the radon release 10 to 20 percent low2).

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1) Ebler and van Rhyn, Ber. deutsch. Chem. Ges. 54, B, 2896, (1921); 44, 2322, (1921); Zeit. anorg. Chem., 73, 1, (1911).

2) Lind and Whittemore, U.S. Bureau of Mines Tech. Paper 88, (1915), p.1

A careful and praiseworthy investigation of the chemical methods necessary to completely dissolve a rock has been made by C. N. Fenner[1]. The technique is particularly laborious for euxenites and monazites which contain quantities of titanium, tantalum and columbium oxides. Frequently 3 to 4 days work are required to dissolve a sample.

Paneth, Urry, and Koeck[2,3], and Quirke and Finkelstein[4] have dissolved their iron meteorites in HCl alone, a method permitted by the absence of silicates.

3. THE DIRECT FUSION METHOD

A method for removing radon from rocks (or other solids) which avoids the limitations of the solution and the carbonate fusion methods has been developed. A speciman of the rock is ground to pass a 60 mesh screen and this powder is placed in a horizontal graphite "U" bar or trough which is both the crucible and the resistor in a special high temperature, low vacuum, electric resistance furnace described on pp. 18 to 25. No flux nor other material of any sort is added. The furnace is heated for 150 seconds and reaches over 1800°C. This fuses the rock completely. Some of the constituents, such as the feldspars, which melt at about 1100°C, boil vigorously above 1400°C and these act as solvents for the higher melting constituents. The chemical constituents of the rocks react with each other giving off gaseous products at a rate of about 0.001 mols per minute per gram of rock. This is an intra-granular gas washing process which speedily sweeps out the last traces of radon from the interstices of the rock and is more intimate than the inter-granular

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1) C. N. Fenner, Am. Jour. Sci., 16, 369, (1928); 16, 382, (1928).
2) Paneth and Koeck, Zeit. f. Phy. Ch. Bodenstein Festband, (1931), p.145.
3) Paneth and Urry, Z. Phy. Ch., (A), 152, 127, (1931).
4) Quirke and Finkelstein, Am. Jour. Sci., 44, 237, (1917).

gas washing action of CO_2 in the carbonate fusion process. The appearance of a typical biotite granite after fusion is shown in Figs. 3 and 4a,b,c, pp.19a & 19b. Note the volcanic appearance of the fused mass, due to the release of gaseous products.

This method suggested itself on reading the interesting report of Fletcher[1], who roasted splinters of pitchblend weighing from 0.01 to 0.0001 gm. in a micro-furnace using 10 amps. per sq. mm. of graphite resistor cross section. Fletcher claimed complete deemanation of his samples in 1 minute at full redness (900°C). In the light of present results this condition is insufficient to deemanate carnotite or granite, but with a large furnace capable of raising several grams of rock to twice this temperature the direct method has produced excellent results. Other direct roasting experiments are confined to the work on radium salts or ores by Kolowrat[2] and Lind and Whittemore[3]. No treatment of ordinary rocks by this method antedates this research.

4. DESCRIPTION OF APPARATUS FOR THE DIRECT FUSION METHOD

a. THE FURNACE

The furnace[4] finally developed for this work is shown in Figs. 5 and 6, p. 20. It is assembled on a horizontal steel baseplate 13 in. x 4 in. x 1/2 in. This plate is water cooled through 4 1/4 in. copper tubes soldered to its bottom face. The two hollow copper electrodes are spaced 9 in. between centers. They are 2 in. x 1 in. x 1/2 in. and are water cooled through copper tubes which lead down through the base plate.

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1) Fletcher, Phil. Mag., 26, 674, (1913).
2) Kolowrat, Le Radium, 4, 317, (1917); 6, 321, (1909); 7, 266, (1910).
3) Lind and Whittemore, U.S. Bureau of Mines Tech. Paper 88, (1915), p.16.
4) Two earlier furnaces are described in appendix A.

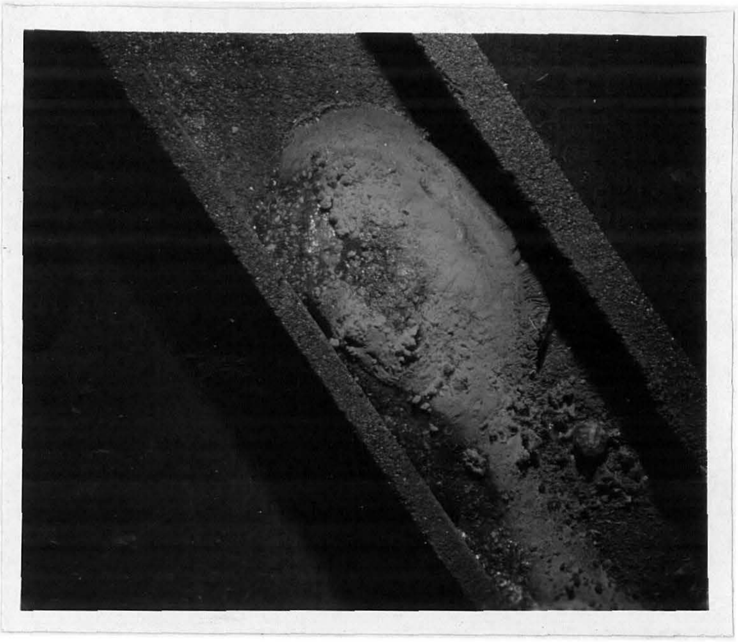

Fig. 3. Appearance of a granite charge after two runs at 1770°C. (X3)

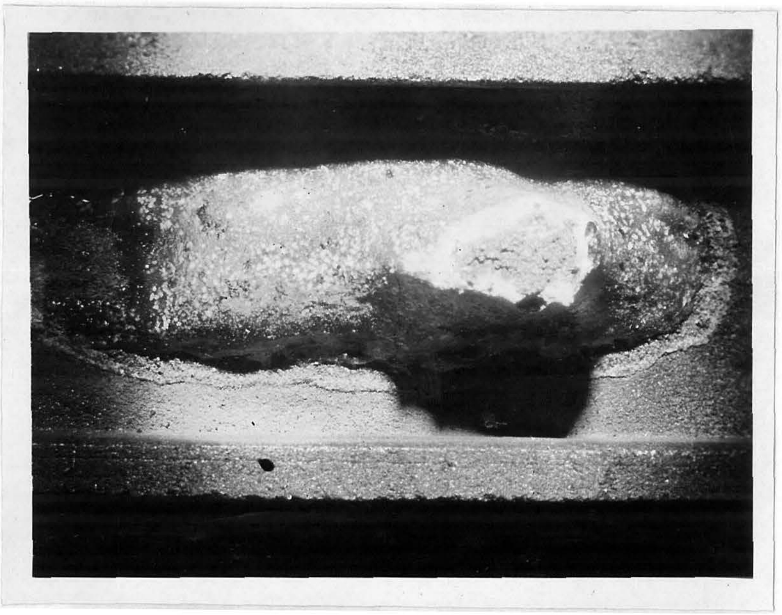

Fig. 4a. Typical appearance of a granite sample after fusion. Note coalescence of the fused mass. Temp. 1710°C. (X3)

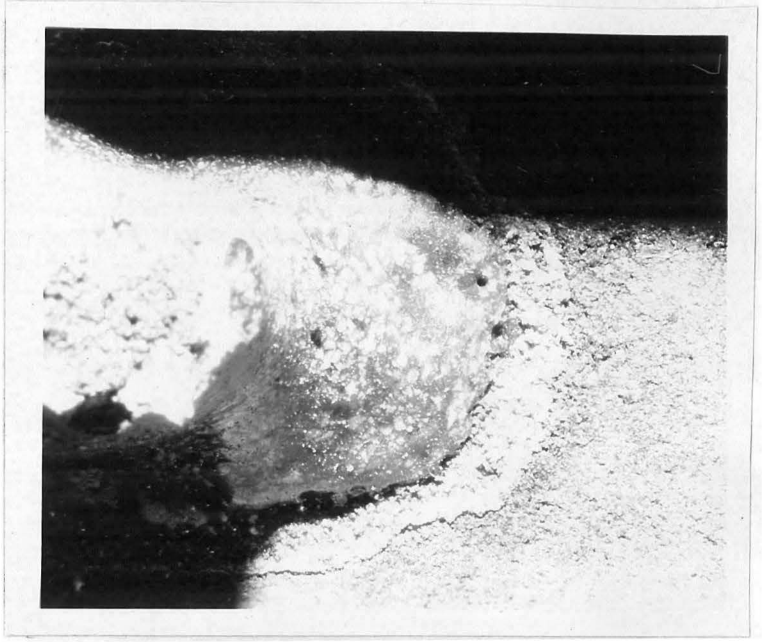

Fig. 4b. Enlargement of right end of Fig. 4a, Note volcanism, and slight chemical action at the granite-graphite junction. (X7)

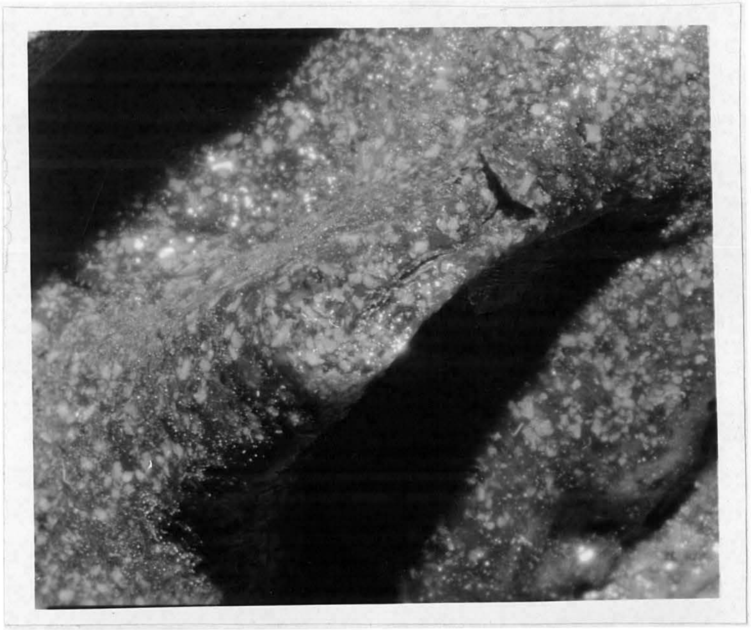

Fig. 4c. Enlargement of a region of a granite mound near that of Fig. 4a. Under higher magnification the volcanic fissure in the center is seen to be lined with secondary crystals. (X9)

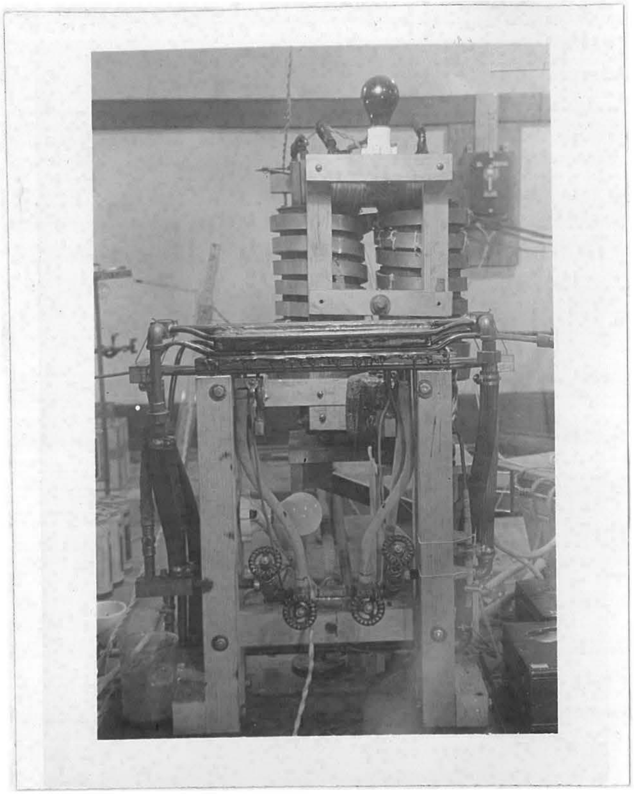

Fig. 5. Furnace unit assembly.

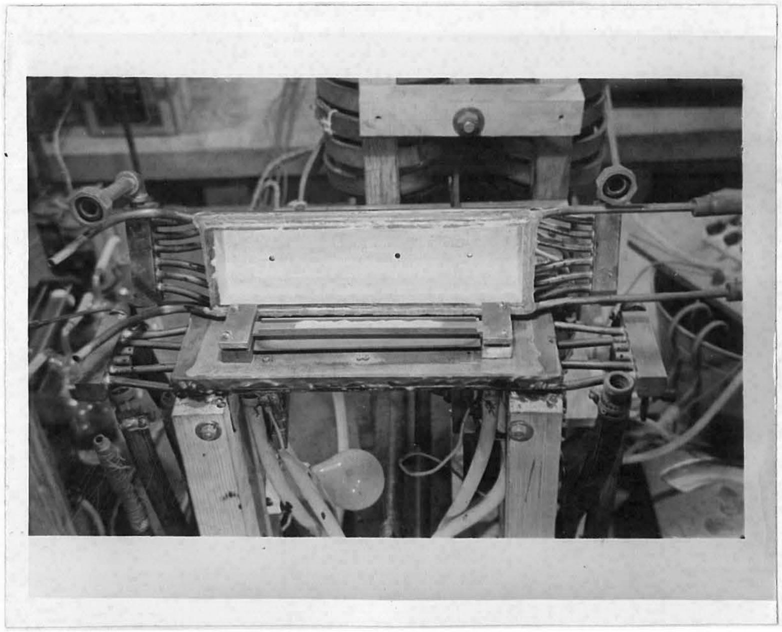

Fig. 6. Furnace, with cover tipped back and upper radiation screen removed to show a rock sample in the trough electrode.

These tubes are silver soldered into the electrodes, and carry both the cooling water and the heavy electric current to the electrodes. The electrode units are insulated from the base plate by paper insulators immersed in well run-in, hard, banker's specie wax, which also provides the vacuum seal.

The resistor-crucible is an Acheson graphite trough as shown in Fig. 6, p. 20. It is clamped to the electrode by a 2 in. x 1 in. x 1/4 in. copper block held by two brass machine screws. These screws are pulled down "finger-tight". This allows gliding of the resistor in the clamps to accomodate its large expansion at high temperature. The contact resistance is about 0.001 ohm and is steady in value. The 1/2 in. wide trough resistor has a resistance of 0.065 ohms, and consumes 7.5 kilowatts at 22 volts and about 340 amperes. Its volumetric capacity is about 4 gm. of ordinary rock, which is never placed closer than 1 inch to the electrode clamps. The side walls on the resistor are necessary where temperatures over 900°C are used because a silica crystal structure transformation at about 950°C causes the powdered rock to jump like pop corn; these walls prevent the rock from dancing off the sides of the resistor.

Calibration curves of equilibrium temperature vs. (a) watts input (b) watts per inch of perimeter of cross section of the trough resistors (c) time of heating, are given in Figs. 7, p. 22, 8 and 9, p. 23. Fig. 8 allows the temperature of bars of widths other than the standard sizes of 1/2 in. and 1 in. wide to be closely estimated from the measured power input. It is based on the observed fact that for a given temperature the watts per sq. in. of total exposed resistor area is nearly constant for all widths of resistors. Since the resistor length is always 8 in., the perimeter is proportional to the total exposed surface. Fig. 9

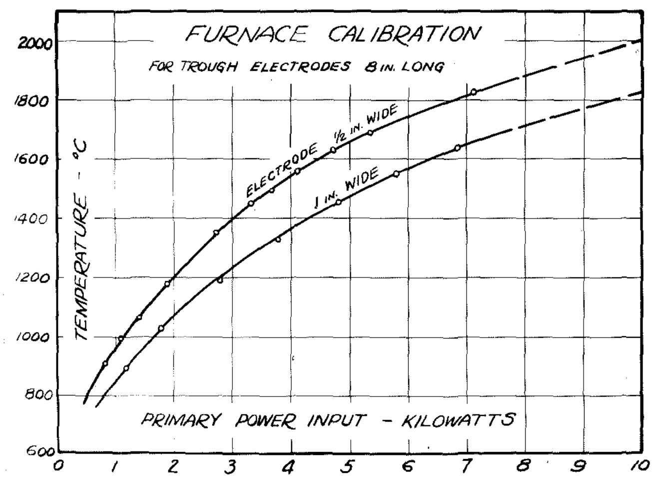

Fig. 7. Temperature calibration of the furnace. These curves are quite accurately represented by the equation $T = aW^n$, where T is degrees centigrade, W is power in watts, and for the $\frac{1}{2}$ in. electrode a = 960, n = 0.337, while for the 1 in. electrode a = 840, n = 0.350.

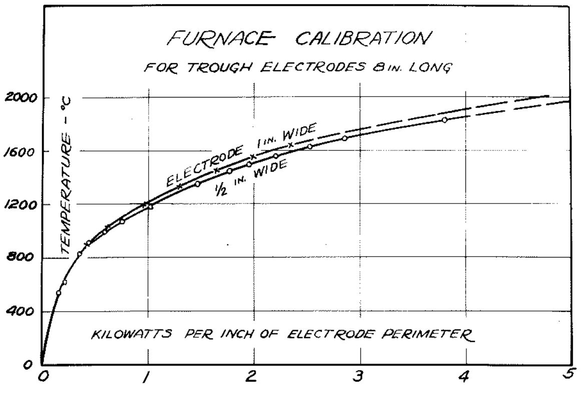

Fig. 8. Furnace calibration curve from which temperature can be estimated for any electrode width.

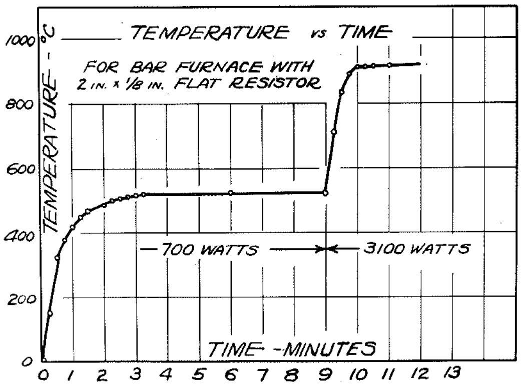

Fig. 9. Temperature-time response curve showing how quickly the furnace comes up to temperature.

represents temperatures low enough to be measured thermoelectrically. The temperature-time curves for higher temperatures cannot be accurately obtained with the optical pyrometer because of the time required for matching colors. However Fig. 7, p. 22 indicates that at high temperatures, equilibrium is reached sooner than at low temperatures, and optical pyrometry has shown that with 7 K.W. input the furnace comes to within 60°C of equilibrium temperature in 45 sec., and within 30°C in 1 min. when started cold.

The lower radiation screen consists of a sheet of graphite 7 3/4 in. x 1 1/2 in. x 1/8 in., it is supported by two 3/16 in. lavite blocks in a horizontal position under the resistor. A similar, slightly longer graphite sheet rests on thin mica insulators on top of the electrode clamps, and is the upper radiation screen. These screens, being non-reflecting, conserve heat principally by their thermal resistance. Their presence raises the temperature of the resistor by about 70°C at 1000°C.

Various minerals and oxides are distilled out of the rock during the run. These condense principally on the two radiation screens, thus relieving the furnace walls of this deposit. New screens and resistor are used for each run.

The furnace cover is 11 in. x 2 1/2 in. x 1 1/4 in inside. It is machined from a length of 3 in. channel bar, the ends being closed by steel plates 1/4 in. thick, brazed in position. It is coated inside with aluminum, painted on in powdered form with a water glass binder. One inch off center, and on the longitudinal axis of the furnace, a 3/16 in. hole leads through a water cooled 1 in. x 1 in. x 5/8 in. brass block soldered to the outside of the cover. This hole is covered by a square of microscope slide glass fastened to the brass block with deKhotinsky cement, and is used for optical pyrometer measurements of the resistor temperature as seen through a 1/4 in. hole in the upper radiation screen.

For low temperatures (below 1000°C) the furnace was calibrated against both Pt-PtRh and Chromel-Alumel thermocouples, led through the base plate in porcelain sleeves, vacuum sealed with insulute coated with glyptal. For continuous temperature readings a Leeds-Northrup wall galvanometer, with about 14,000 ohms in series with it, was read with a straight filament lamp and a semi-transparent scale calibrated directly in degrees Centigrade.

To the outside of the cover, which is 1/8" thick, are soldered 8 1/4" copper tubes carrying cooling water. Two of these tubes are at the bottom edge of the cover, where it rests on the base plate. The vacuum seal is a fillet of bee's-wax resin mixture joining this cold tube to the cooled base plate. Even though this wax melts at 40°C, it shows no signs of softening during 12 minutes operation of the furnace at 2000°C, a far more severe test than the ordinary 150 second run.

Separate 1/4" globe valves, located directly under the furnace, control the flow of cooling water to the furnace cover, base plate and the two electrodes. A rapid flow, with only a few degrees of water heating, is maintained during the run and for 5 minutes thereafter while the furnace cools to room temperature.

Resistors of any width up to 2 inches may be used in this furnace A 1 1/2 in. special trough resistor has been made which can be used to investigate the temperature-time-radon removal relations for the carbonate fusion method, a research to which this furnace is also well adapted.

b. POWER SUPPLY

The 2300 volt secondary of a 10 K.W., 110-220 volt primary, line transformer was removed, and replaced by 16 turns of a copper conductor consisting of 4 1/16 in. x 1 in. bus bars laid together to form a single conductor 1/4 in. x 1 in. in cross section. The secondary is one layer deep, 8 turns on each leg, and has no special devices for cooling other than normal heat loss to the room. It is mounted without a case directly behind the furnace to allow short 1 in. x 1/2 in. bus bar connections to the furnace to be made. No heating of the secondary is observable at 400 amperes, and 1000 amperes can be drawn for a limited time. The voltage step down ratio is 1 to 10; the overall efficiency 95%.

c. POWER CONTROL

The secondary voltage applied to the furnace is regulated by a water immersed resistance in the transformer primary circuit. This consists of a single resistor of 1/4 in. x 32 ga. nichrome ribbon, nailed to two wooden platforms and the whole water immersed. The total resistance is 4.075 ohms, and this is divided into 8 sections of 0.025, 0.05, 0.1, 0.2, 0.2, 0.5, 1.0, and 2.0 ohms each, by brass clamps fastened to the nichrome ribbon. These section taps lead to 8 knife switches by which any sections may be shorted out. By combination of these 8 resistances, like a set of balance weights, any primary resistance from 0.025 to 4.075 ohms, in 0.025 ohm steps, can be obtained. The resistor mounting platforms are immersed in water in a small galvanized iron tub, fed by the cooling water from the furnace electrodes and drained to the sink by outlets 1 inch below the top rim of the tub.

This rheostat, originally designed merely for preliminary work, has been in constant use for three years without requiring any attention. It will absorb 5 K.W. at 50 amperes continuously without noticeable heating.

d. ION TRAP

When rocks are boiled in the furnace, the high temperature and chemical activity of the melt occasion the release of about 0.001 mols of gas per gm. of rock per minute. Much of this gas is ionized, and if these ions are allowed to enter the ionization chamber an abnormally high discharge occurs which does not completely disappear for 3 hours. These ions can be removed from the gas stream electrostatically without in any way influencing the free passage of radon or thoron atoms.

The ion trap consists of two brass plates 1 1/2 in. wide by 5 in. long spaced 1 mm. apart by narrow bakelite spacers held at the edges of the plates by beeswax and resin, which also provides the vacuum seal. The ends of the plates are drilled to take glass tubing. This simple assembly presents to the gas stream a rectangular cross section with a field strength of 2500 volts per cm. supplied by the 250 volt electrometer charging battery. Each run causes a visible white deposit in the ion trap.

The curves of Fig. 10, p. 28, contrast the discharge of the electrometer in a run without the ion trap with an identical run using the trap. The sharp initial ionization rate seen in both curves is attributed to thoron. This is entirely gone in 20 minutes, after which the curve taken with the ion trap shows the normal increase in slope caused by the building up of the decay products of radon. Equilibrium is correctly reached after 2.5 hours and the curve becomes a straight line, indicating a constant discharge rate of the electrometer.

The other curve, however, shows an abnormally high ionization which gradually decreases for 3 hours when all the heavy ions have reached the walls; then the straight line slope conforms to the radon

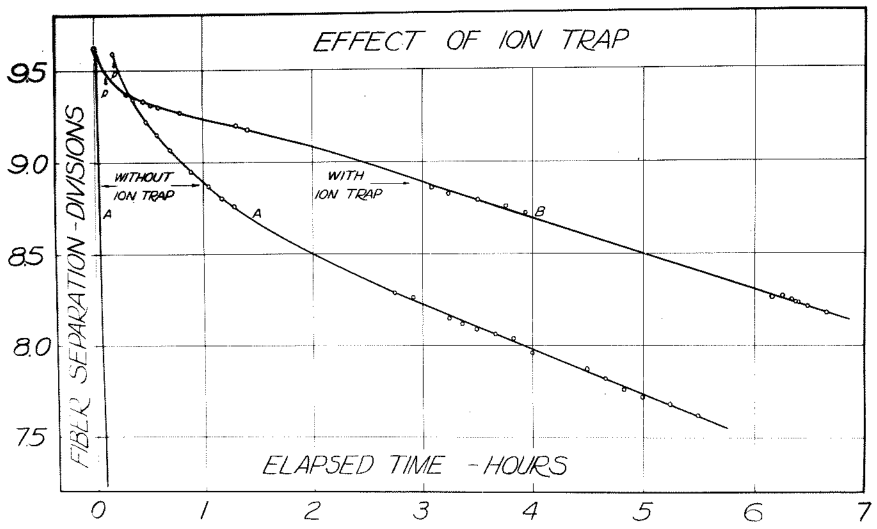

Fig. 10. Curves A and B show the electrometer fiber separation during two runs described below. The curves A are from radon boiled out of 3.114 gm. of biotite granite in 150 sec. at 1840°C. The gases from the furnace were passed through fresh H_2SO_4 in the micro-cell. The nearly vertical branch of curve A shows that the electrometer was completely discharged by ions during the first few minutes. It was recharged and curve A continued 10 min. after the beginning of the run. All the ions were not swept out until about 2.5 hours had elapsed.

Curve B shows the entire ionization curve due to the radon from 2.053 gm. biotite granite boiled 150 sec. at 1800°C. The furnace gases were passed through glass wool and the ion trap only. The high initial current due to ions is absent. The steep beginning of the curve is ascribed to thoron.

In both curves the point P shows when the ionization chamber filling with CO_2 was completed. The diameter of the circles represents the observational uncertainty.

and decay products ionization. Here the effects due to radon and its products have been masked for 3 hours by the slow sweeping out of heavy ions. The ion trap prevents such spurious effects.

e. DRYING AGENTS, ETC.

The gas line to the furnace contains only two apparatus; a 2 cm. bulb containing a tuft of glass wool, and the ion trap. The sodium hydroxide solution, phosphorus pentoxide tube, sulfuric acid micro-cell, and mercury sealed gas reservoir formerly used by McMillan[1], Piggot[2] and others are eliminated. This is achieved by the use of CO_2 as background gas and by the insulation "drying room" in the ionization chamber.

f. TECHNIQUE OF OPERATION

The rock sample to be tested is ground to pass a 60 mesh wire screen. Three to four grams are weighed out and placed in a fresh graphite trough resistor in the furnace. The graphite radiation screens are put in place and the furnace closed and sealed with a mixture of beeswax and resin. The cooling water is turned on and the entire system - ionization chamber, ion trap, and furnace - evacuated to less than 1 mm. Hg. The system then stands evacuated for 5 min. and if no vacuum leak is observed the run is begun. With 3.0 ohms in series with the transformer primary, 220 volts are thrown on. After 90 seconds operation the 3 ohm primary resistance is shorted out and the full 220 volts applied for the remaining 60 seconds. Under these conditions the furnace consumes 7 kilowatts and reaches 1800°C. The furnace is shut down and the entire system is brought to atmospheric pressure with tanked CO_2 introduced through the furnace. This has been shown to sweep all the radon

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1) McMillan, M.S. Thesis C.I.T., (1929).
2) Piggot, Am. Jour. Sci., <u>17</u>, 15, (1929).

into the ionization chamber, which is then isolated by a stopcock, and readings taken on it as described on pp. 55 to 58. Readings of primary and secondary voltage and current as well as the gas pressure in the system are taken during the furnace run. A schematic diagram of the apparatus is shown in Fig. 11, p. 31.

5. RADON RELEASE FROM CARNOTITE AS A FUNCTION OF TEMPERATURE.

Fletcher[1)] reported complete deemanation of pitchblende splinters in one minute at 900°C. Kolowrat[2)] demonstrated complete radon removal from Ba-Ra salts at 1200°C. Lind and Whitemore[3)] claimed deemanation of carnotite ores below the fusion point of Jena glass. The results now to be described indicate that the last authors may have been under a misapprehension regarding the completion of removal of the radon.

Fig. 12, p. 31, shows the temperature dependence of radon removal from directly heated carnotite. The curve indicates that complete deemanation occurs at about 1600°C. A detailed discussion of these results is presented in the chapter on the absolute radium calibration of the electrometer.

6. RADON RELEASE FROM BIOTITE GRANITE AS A FUNCTION OF TEMPERATURE

Fig. 13, p. 32, presents the principal results of a systematic study of the temperature dependence of the release of radon from uniform samples of a biotite granite.

In this set of 24 determinations the sulfuric acid cell described on p. 13 was the only apparatus in the gas circuit from the furnace to the ionization chambers. It was believed that this cell was unable to

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1) Fletcher, Phil. Mag., <u>26</u>, 674, (1913).
2) Kolowrat, Le Radium, <u>4</u>, 317, (1907); <u>6</u>, 321, (1909); <u>7</u>, 266, (1910).
3) Lind and Whitemore, U.S. Bureau of Mines Tech. Paper 88, (1915); Jour. Am. Chem. Soc., <u>36</u>, 2066, (1914).

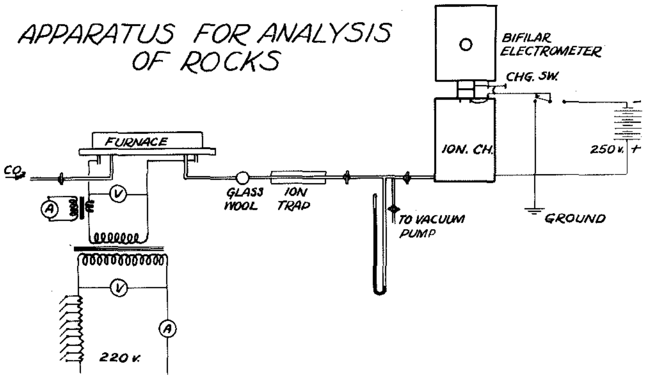

Fig. 11. Schematic diagram of apparatus for removal of radon from rocks.

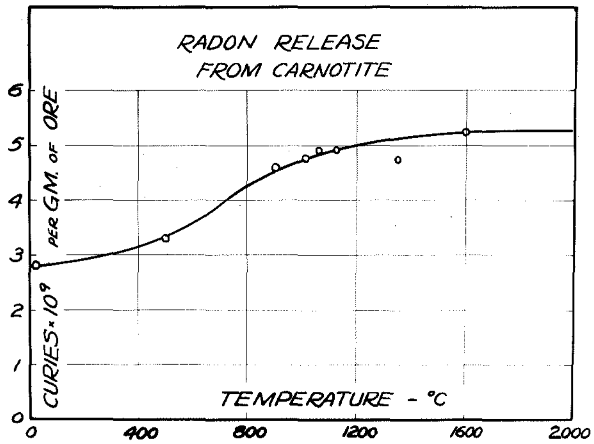

Fig. 12. Radon release from carnotite ore as a function of temperature.

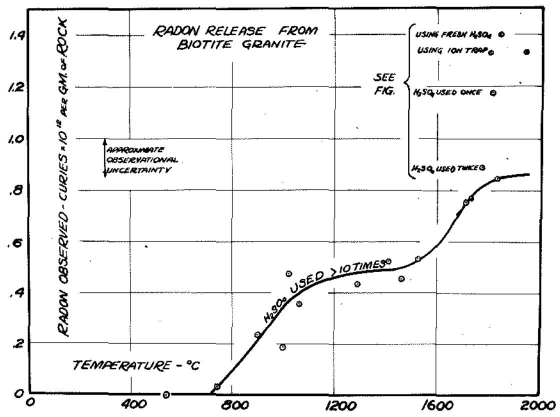

Fig. 13. Radon release from biotite granite as a function of temperature.

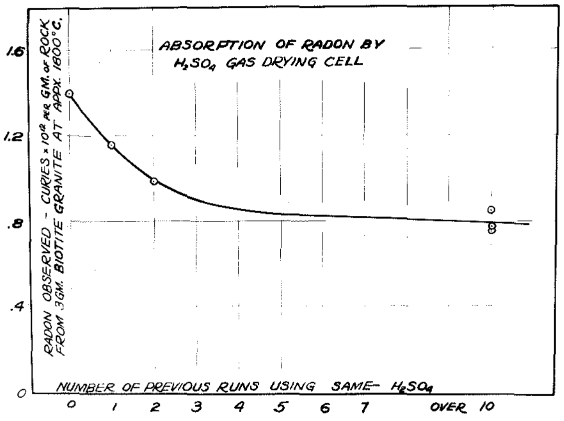

Fig. 14. Hold-up of radon in H_2SO_4 micro-cell shown in Figs. 1 and 2, p. 12, showing why it must not be used in the analysis of rocks, due to the action of furnace vapors on the acid.

retain any of the radon passed through it, since this was true when the cell was used with water samples, and that therefore only one variable, temperature, was being studied. However the last five determinations of this series clearly proved that the cell should not be used with the furnace. Fig. 14, p. 32, shows the amount of radon which succeeded in passing through the cell to the ionization chamber in successive runs, beginning with fresh C.P. conc. H_2SO_4, and holding all other conditions invariant throughout the series. During each determination of this series the sulfuric acid was slightly darkened. This is now believed due to the deposition of carbon in the acid as a result of chemical action on the gases liberated from the rock in the furnace. It is also possible that the boiling of the granite produced some SiF_4, which is a gaseous product, and that this reacted in the cell to precipitate silica gel, according to the formula $2\ SiF_4 + 2H_2O = H_2SiF_6 + SiO_2 + 2HF$. Regardless of the chemical hypothesis adopted, there is unambiguous physical evidence that during each run the sulfuric acid cell became a better adsorbent of radon.

The experimental points on Fig. 13, p. 32, must therefore be regarded only as relative values. The general form of the curve, particularly the temporary maximum between 1200° and 1400°C are real effects independent of the acid cell action because the sequence of tests was not one of ascending temperatures, but rather alternated between high and low temperature runs.

Upon replacing the cell by a tuft of glass wool and the ion trap already described, the radon reaching the ionization chamber returned to the maximum value obtained using fresh acid.

To check the efficacy of 1800°C the last sample tested using the ion trap was immediately retested at 1900°C, and no traces of further radon were obtained. There are but two possible interpretations of this result. Either the heating to 1800°C and the subsequent cooling altered the sample in such a fashion as to prevent the further removal of radon by the same or higher temperature, or the 1800°C heating removed the radon completely. There is no evidence to support the former view and we must regard 1800°C as a temperature which completely deemanates this granite. This material is that designated specimen No. 1 by McMillen[1], who determined its radium content by his carbonate fusion method as 1.25×10^{-12} gm. radium per gm. rock. The direct fusion method has found 1.4×10^{-12} gm. radium per gm. rock using the same radium standards for the calibration of the electroscope.

There is no question regarding the general shape of the temperature-radon release curve and it is clearly demonstrated that 1200°C is entirely inadequate to effect complete deemanation of ordinary rocks, while 1800°C accomplishes this end. This is the state of the experiments on granite rocks at the moment of writing. As the present rock sample is nearly exhausted the curve of Fig. 13, p. 32, will not be redetermined. Several new rock samples are being prepared to determine the temperature-percent radon removal relationship in rocks of varying acidity. In these tests only a tuft of glass wool and the ion trap will separate the furnace from the ionization chambers.

7. RADON RELEASE AS A FUNCTION OF TIME OF HEATING

Because about one minute is required for the furnace to come up to temperature after turning on the power, the shortest runs used have been 150 seconds. The time dependence of radon removal was tested by

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[1] McMillan, M.S. Thesis C.I.T., (1929).

two methods.

1. Samples were run in the ordinary way for, say, 5 minutes, then allowed to cool and immediately rerun at the same temperature for an additional period of, say, 10 minutes. The radon obtained in the second heating was measured in a second ionization chamber. In no case has any additional radon been removed from a rock after an initial run of 150 seconds or more.

2. Samples were run for prolonged periods and the radon release compared with the release in a short time at the same temperature. Heating for 1 hr. 15 min. at 1160°C removes no more radon than a 150 second heating at the same temperature.

It is established that direct heating for 150 seconds removes all the radon that can be removed at any given temperature. A shorter time might achieve the same result, but there is no practical reason for farther shortening of the furnace runs. It is of interest to recall that using the carbonate fusion method the usual time of heating is one hour or more.

8. RADON RELEASE AS A FUNCTION OF SIZE OF SAMPLE GRAINS

It is generally agreed that very fine grinding of rock samples may release some of the radon to the air. The most recent quantative work bearing on this belief is an investigation by Piggot and Merwin[1]) who separated the various mineral constituents of two granite rocks and found the radium to be chiefly associated with the mica. Hot water leaching of ground samples of the original granite removed from 0 to 34% of the radon, but none of the radium. It is therefore indicated that the radon, to a limited degree at least, occupies the interstices be-

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1) Piggot and Merwin, Am. Jour. Sci., 23, 49, Jan. 1932.

tween the mineral grains in the granite.

McMillan[1] found the emanating power of a very finely ground shale to be negligible. The biotite granite used in the present work for determining the temperature and time dependence of radon release was ground to pass a 60 mesh screen. It is safe to assume that no radon escapes from this rock at room temperature. It has just been shown that about 1800°C is required for complete deemanation; this is above the fusion point of the rock and hence the size of grinding of the original sample plays no role except that of providing an easily handled, well mixed, homogeneous sample. Grinding to pass a 60 mesh screen is entirely satisfactory.

9. ARTIFICIAL PRODUCTION OF CERTAIN MINERALS

Some of the crystals grown on the radiation screens during furnace runs are of great mineralogical interest. Cristobalite, and certain other minerals have been tentatively identified, and micro-chemical analyses of the opaque crystals, which cannot be identified under the petgraphic microscope, are being carried out by members of the geology department. The first artificial production of cristobalite is believed to be found here. Figs. 15 to 20, pp. 37, 38, 39, are photomicrographs of some of the most interesting types of crystal growths.

At high temperatures the reversible reaction

$$2C + SiO_2 \rightleftarrows SiC + CO_2$$

probably takes place between the resistor and the silica in the rock. There are definite localized deposits of carbon near the individual fused rock masses and hence we must infer that this reaction has indeed been going to the left as well as to the right; and that therefore crystalline silica growths, such as cristobalite, are to be expected.

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[1] McMillan, M.S. Thesis, C.I.T. 1929, p. 19.

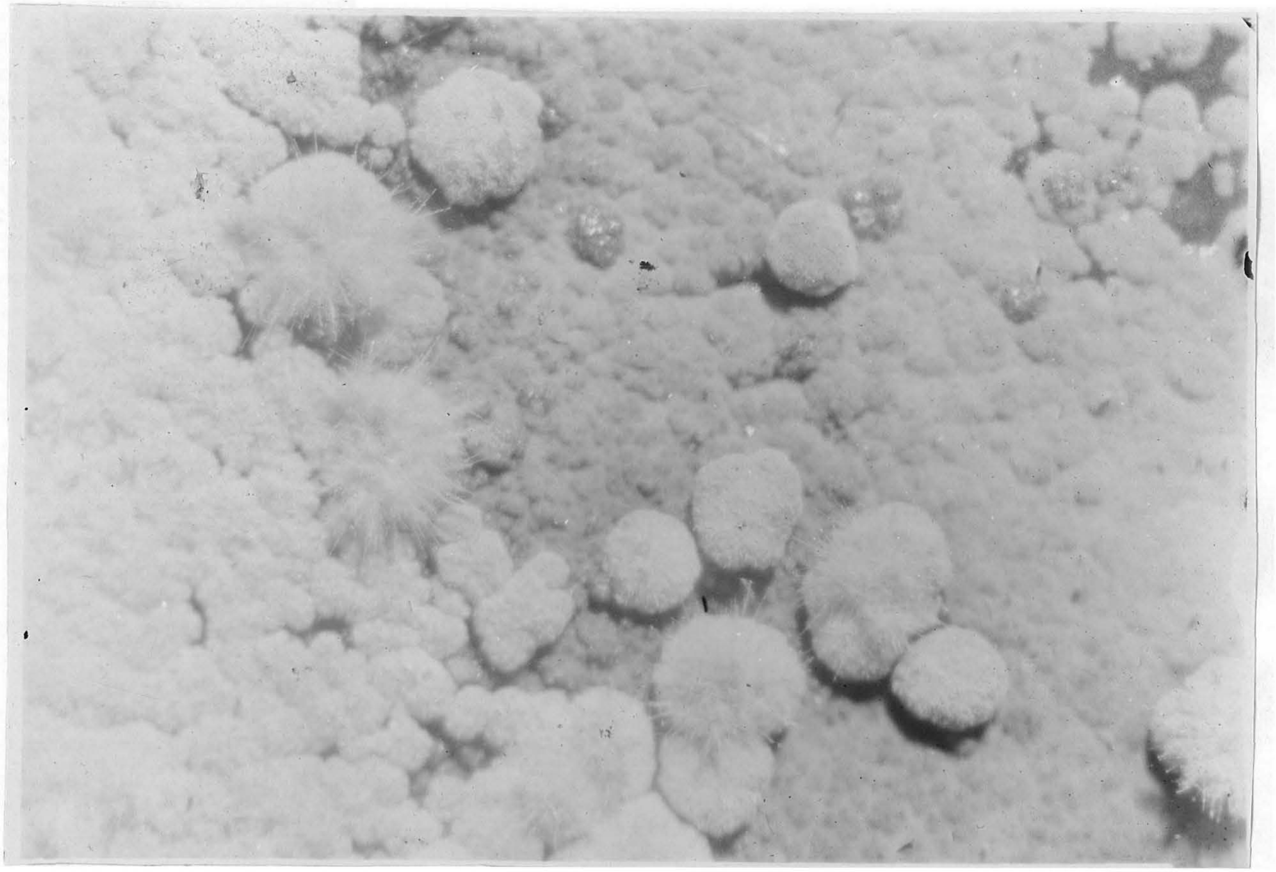

Fig. 15. Crystalline growth on radiation screen above fusion shown in Figs. 4a,b,c. (X75)

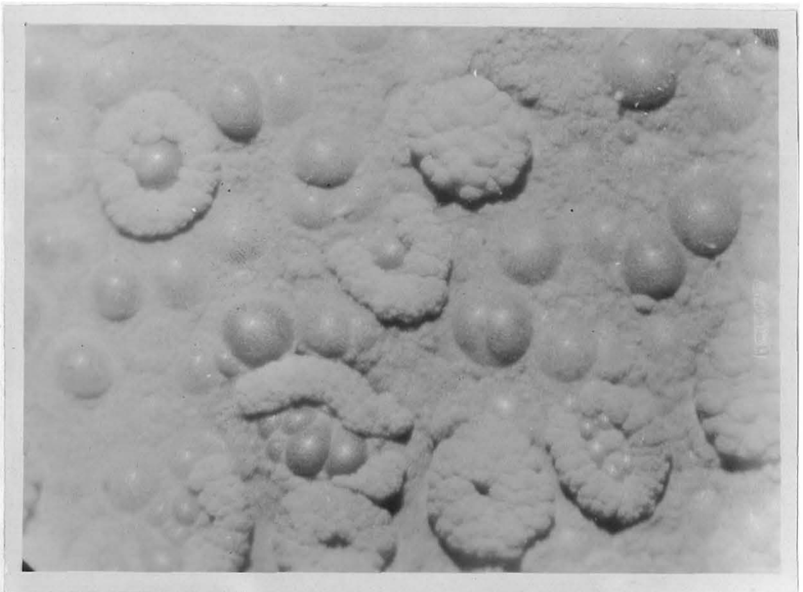

Fig. 16. Crystalline growth above the fusion of Fig.3. The grapelike clusters are believed to be cristobalite, the smooth domes glass. (X75)

For preparing Figs.3,4,15 to 20, I am indebted to the kindness of Mr. George Anderson.

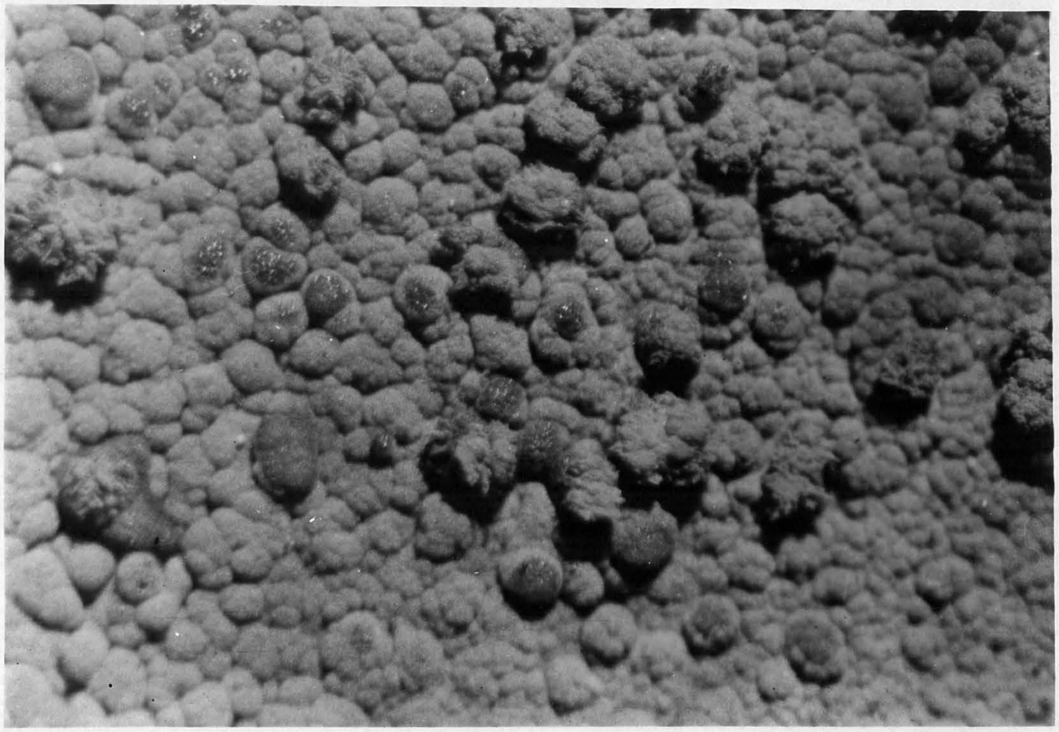

Fig. 17. Crystalline deposit from granite at 1940°C. Note spur like growths at center and left, and superposed growths at center. (X75)

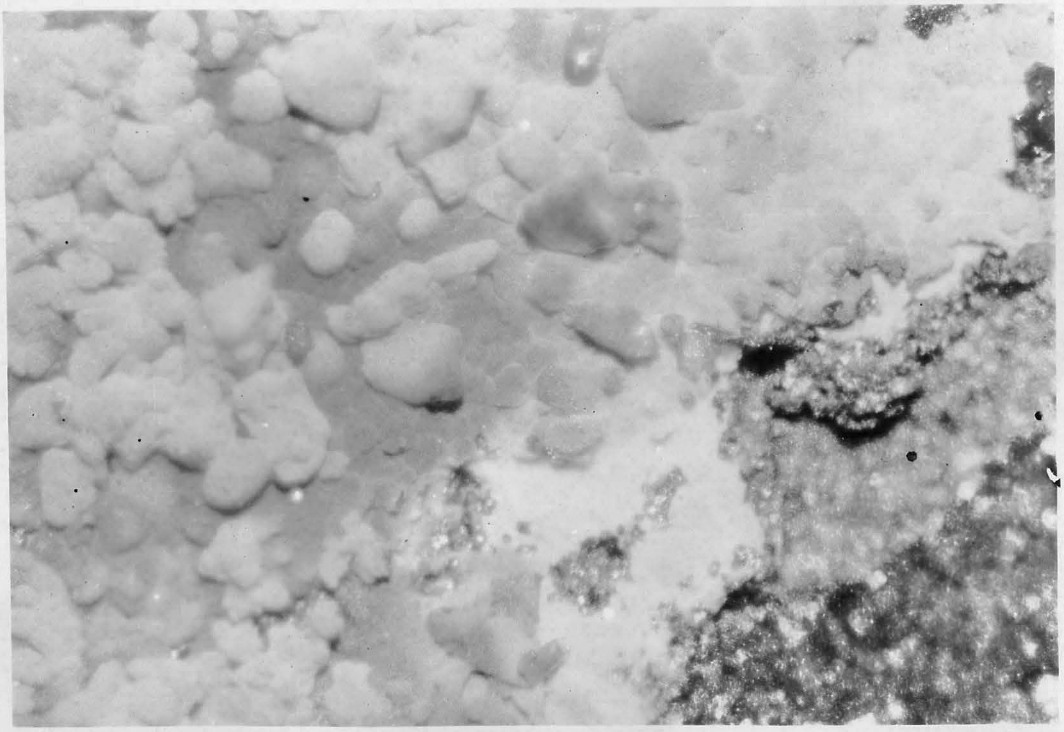

Fig. 18. Region near that of Fig. 17. Note very fine grained deposit in lower center. (X75)

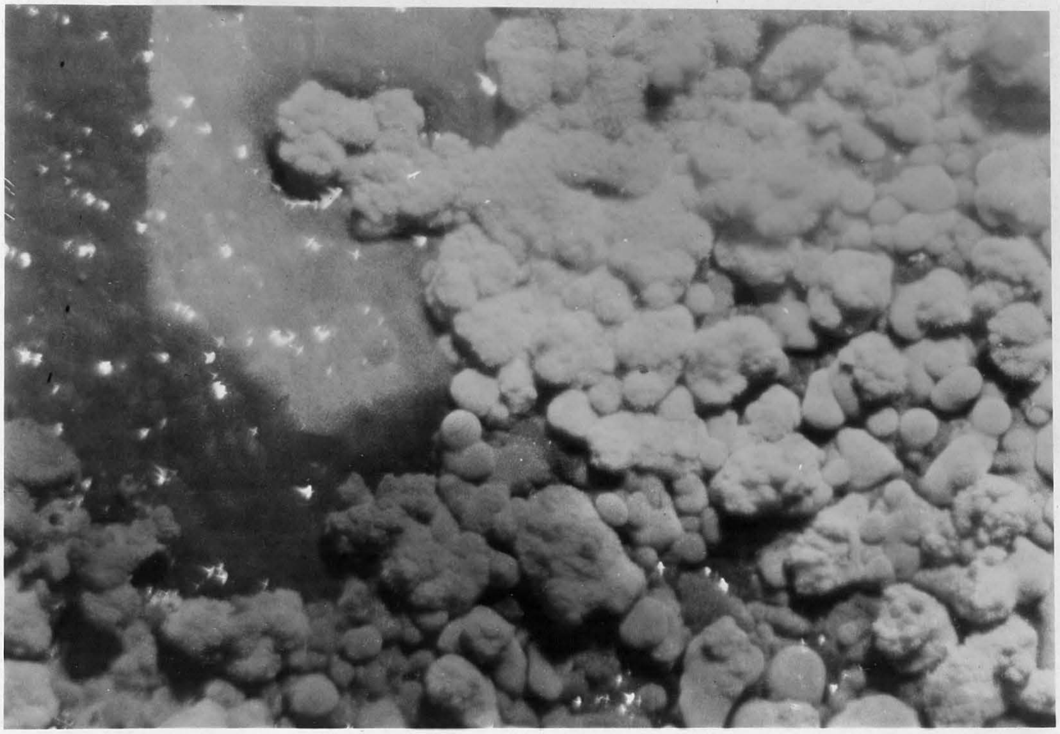

Fig. 19. Region near those of Fig. 17, 18 showing a glassy structure at upper left, and a glassy sphere overgrown with cristobalite(?). (X75).

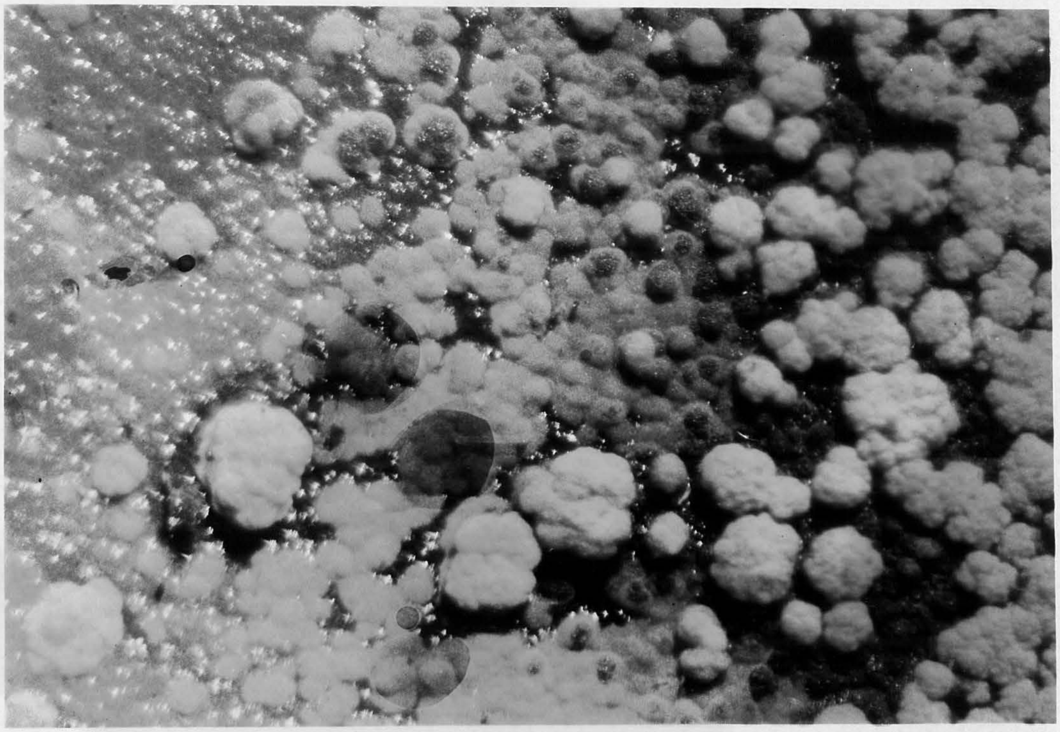

Fig. 20. Region near that of Fig.15, showing entirely different structure. Note glassy deposits at left, and glassy spheres overgrown with cristobalite(?) at center. (X75)

II. THE MEASUREMENT OF SMALL QUANTITIES OF RADON

INTRODUCTION

The minute quantities of radon involved in these measurements are detected by the ionization produced by their alpha particles in an emanation electroscope. The beta and gamma radiations produce only about 0.3% of the observed ionization.

A. ANALYSIS OF THE BACKGROUND IONIZATION

1. IMPORTANCE OF ACCURATE KNOWLEDGE OF THE BACKGROUND

The ionization observed in a chamber containing radon and its decay products is made up of two parts, the radioactive ionization and the background, sometimes called the residual ionization or the zero leak. In the analysis of rocks of very low activity the background may be even larger than the ionization due to the radon from the rock. Thus in the work of Paneth and Koeck[1] the background was often 15 times the ionization due to radon from meteorite samples. In general, the background is approximately equivalent to the activity of 3 gm. of ordinary granite.

Any claim at precision measurements of radon therefore presupposes an accurate knowledge of both the average value of the background and the average deviations to be expected on statistical grounds.

2. STATISTICAL VARIATIONS OF THE BACKGROUND

The importance of the variations in the background has heretofore been generally overlooked in this field. It is clear that the average background can be accurately determined by extended runs, and it is therefore the variations in the background which impose the ultimate natural

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[1] Paneth and Koeck, Zeit. f. Phy. Ch. Bodenstein Festband, (1931).

observation limit, and determine the possible precision of the measurements of small quantities of radon[1].

The ionization due to the alpha particles from radon and its decay products obeys statistical laws, and it is possible to speak of an average or mean value of this ionization. Feather[2] and others have shown that the distribution in time of the emission of alpha particles is purely random, and Bateman[3] has shown that the mean error or variation to be expected in the emission during any time interval is $Z^{1/2}$, where Z is the average number of particles emitted during this time interval.

Probably the background also conforms to these statistical laws and it is therefore possible to compute the mean deviation to be expected in the background. The average background in the present ionization chambers is 1.36 x 10^8 ion pairs per hour. If we assume half of this to be due to fast alpha particles, which is not unreasonable, we find a theoretical mean deviation in the background of over 2% per hour, whereas if alpha particles were responsible for all the background the mean deviation would be 4% of the background per hour. Obviously, increasing the time interval decreases this deviation by the square root of the duration of the time interval. Also, decreasing the absolute value of the background will decrease the mean deviation according to the square root law.

The normal background for air in the present apparatus varies between 10.9 and 11.7 ion pairs per cc. per sec., and for CO_2 between 12.5 and 13.5 ion pairs per cc. per sec. (see p.58). This is close to

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1) Evans, Ph. Rev., 39, 1014, (1932).
2) Feather, Ph. Rev., 35, 705, (1930).
3) Bateman, Phil. Mag., 20, 704, (1910).

the minimum attainable without lead shielding from local gamma radiation, as is evident from the work of Wright[1)], Cooke[2)], Bastings[3)], and Paneth and Koeck[4)].

Bastings, in his excellent examination of gamma ray electroscopes reported that the variations in the background amounted to 5 to 10% during normal observation intervals.

Five runs with the hookup described on p. 76 indicated that a variation as high as 5% per hour in one ionization chamber, or 2% over 5 hours might be expected. In one clear case the background, using the bifilar electrometer, decreased 23% for a 2 hour period in the middle of a 16 hour continuous record of the background. This is an isolated and exceptionally high variation, but even these are predicted by statistics.

3. NATURAL OBSERVATION LIMIT

We can now define the natural observation limit as the point at which the mean deviation of the background is equal to the average ionization from the radon present. This observation limit can be pushed further back by:

1. Lead screening[5)] the ionization chambers.
2. Decreasing the size of the ionization chamber, but not enough to seriously shorten the effective length of the radon alpha tracks.

Large rock samples are obviously desirable.

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1) Wright, Phil. Mag., 17, 295, (1909).
2) Cooke, Phil. Mag., 6, 403, (1903).
3) Bastings, Jour. of Sci. Inst., 5, 113, (1928).
4) Paneth and Koeck, Zeit. f. Phy. Ch. Bodenstein Festband, (1931).
5) Rutherford and Cooke, Ph. Rev., 16, 183, (1903).

4. ANALYSIS OF TWENTY POSSIBLE SOURCES OF BACKGROUND IONIZATION

It is important to consider the various sources of background discharge with a view to reducing its absolute value to a minimum. These sources are:

A. Those due to properties of the gas (excluding radon from the sample) used for filling the ionization chamber, which include:

   1. Radon contained in the gas. If air is used radon can be eliminated either by absorbing it in charcoal cooled by liquid air, or by storing the air for about one month before use. If an old tank of CO_2 is used, these precautions are avoided and a completely reproducible background gas provided.
   2. Heavy ions, with low mobility, coming from boiled rocks in the furnace. These are removed by passing the gas through the ion trap described on page 27 . The gradient of 2500 volts per cm. removes all these ions, which otherwise require from 2.5 to 3.5 hours to be swept to the walls of the ionization chamber. See Fig. 10, p. 28.
   3. Ions from drying agents. No dryers are now used between the furnace and the ionization chamber.
   4. Ions from line friction. Only the line between the ion trap and the ionization chamber can supply these ions. They have not been observed.
   5. Ions from the reducing valve of a high pressure CO_2 tank would require 30 minutes to be swept from the ionization chamber, but these too are caught by the ion trap.
   6. Spontaneous ionization of the gas in the ionization chamber. There is no evidence for this effect.

B. Insulation leaks, including:

7. Natural conduction leak. This is less than can be observed in a 5 hour reading.

8. Failure of the insulation due to contamination of the surface by water, H_2SO_4, or other vapors from the furnace or gas dryers. Gas dryers are not used and no failure of the insulation dryer, described on p. 50, to prevent this effect has ever been observed.

9. Electrostatic soaking of the insulator on charging the instrument. This effect is of known magnitude, persists for 20 to 30 minutes, and is easily corrected for.

C. Background in the electrometer:

10. The insulation leak is negligible, as in the ionization chamber, (Par. 7). The humidity effects which prevented Piggot$^{1)}$ from working during the summer are eliminated by the evacuated head.

11. Ionization of the gas in the electrometer. This is avoided by completely evacuating the electrometer.

D. Ionization from the solid material in the ionization chamber, including:

12. Ions from the insulation dryer. The dryer is covered by a grounded wire screen to prevent the escape of ions.

13. Deposition on the metal walls of decay products from the radon and thoron in the atmosphere. The chambers are always kept closed to the atmosphere. Any deposit is on the outside of the chamber, but this is always kept positively charged to retard this deposition.

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1) Piggot, Am. Jour. Sci., 17, 21, (1929).

14. Solid radioactive decay products from the former runs in the chamber. The decay products are always collected on the negatively charged central electrode. Their effect is usually negligible a few hours after pumping out the radon from a run. The very long lived product radium D has negligible activity, but is cleaned off the central electrode periodically by chemical means, or a new electrode can be installed.

15. Presence of radioactive elements as impurities in the metal, which might also lead to the

16. Release of radon or thoron from the metal into the chamber. There is no evidence for these two effects in this apparatus. In a sealed ionization chamber the background shows no increase with time.

17. Release of alpha and beta particles by the walls, either spontaneously or under the influence of external gamma radiation.

E. Penetrating gamma radiation, including:

18. Gamma rays from radioactive bodies in surrounding objects, room walls, earth and atmosphere. These effects must be held as constant as possible.

19. Cosmic radiation. This amounts to about 2.6 ion pairs per cc. per sec.[1)]

F. From accessory apparatus, chiefly

20. Variation of battery voltage. This is eliminated completely by the present hook-up, which uses the battery only as a charging device, and to supply guarding potential, where a small variation is unimportant. (see p.53).

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1) Millikan, Ph. Rev., 39, 397, Feb. 1, 1932.

The observed background is principally due to sources 17, 18, and 19, the other 17 sources being rendered ineffective by the methods described. Of the 11 ion pairs per cc. per sec. background, approximately 2.6 are of cosmic ray origin, and the remainder principally from local gamma radiation and its effect on the walls of the chamber. If desired, the last 2 effects could be separated by equipping a large chamber with an inner wire grid, everywhere more than 8 cm. from the walls of the vessel, and collecting the ions due to gamma rays alone inside this grid, while those due to gamma rays plus secondary alpha and beta particles from the wall are collected outside the grid.

B. DESCRIPTION AND ELECTROSTATIC CALIBRATION OF THE APPARATUS

1. THE ELECTROMETER CONSTRUCTION

Many types of emanation electroscopes have been described.[1] The instrument constructed for the present work employs some features of those due to Linde[2] and to Wulf[3]. A removable, bifilar electrometer is fitted with a collar which provides both complete mechanical support and electrical contact with any one of several separate ionization chambers. Dimensions and details of construction are shown in Fig. 21, p. 48, which is accurately to scale.

Two sputtered quartz fibers, about 10 μ in diameter, are attached to a quartz bow and supported in an invar frame to avoid temperature effects on the fiber tension. This frame is attached to a grease joint in the top of the instrument, through which it can be rotated from outside for microscope focusing. This feature has proved of great practical value. A length of piano wire completes the electrical circuit from the upper end of the fibers to the axial rod which extends through the amber insulated collar on the bottom of the instrument. The mechanically operated, plunger type charging switch is mounted on the bottom of the instrument and contacts the axial rod outside the amber insulator. A thirty power microscope with a 100 division scale in the eyepiece is mounted on the instrument and observes the fibers as illuminated through a 1/4 in. diameter glass window opposite it.

Two glass stopcocks are wax sealed to brass outlets in the electrometer case. The electrometer is always operated evacuated to less

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[1] Meyer and Schweidler, "Radioaktivitat", 1927, p. 301.
[2] Moore and Kithil, Bull. 70, U.S. Bureau of Mines, 1914, p. 66.
[3] Wulf, Phys. Zeit., 8, 246, 527, and 780, (1907).

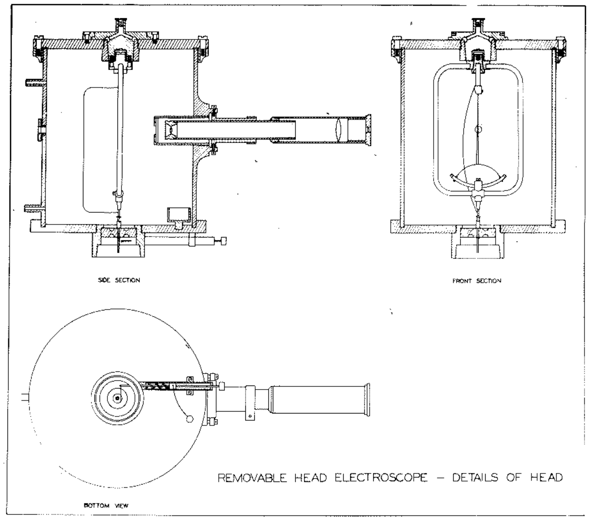

Fig. 21. Construction of bifilar electrometer head showing special grease joint for rotating fiber assembly. See Fig. 22b, p. 48b, for photograph.

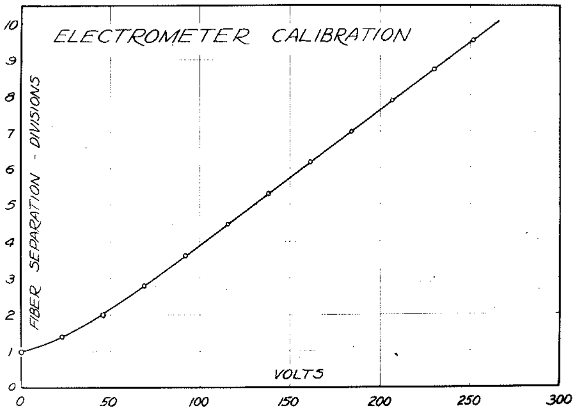

Fig. 22a. Voltage calibration of bifilar electrometer.

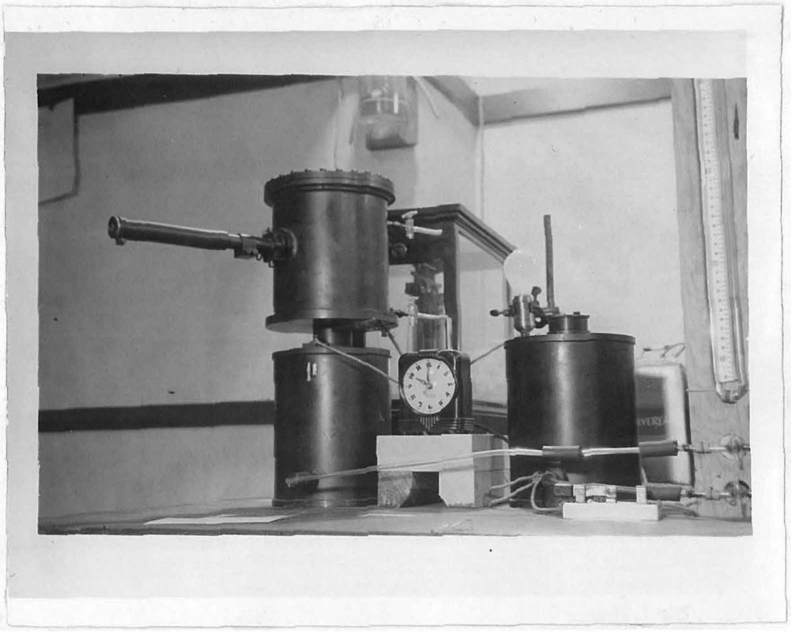

Fig. 22b. Removable head, bifilar electrometer with two ionization chambers.

than 1 mm. No vacuum leak has been observed in nearly three years of continuous use.

There is a small cup containing P_2O_5 screwed to the inside bottom of the case.

2. THE ELECTROMETER CALIBRATION

The fiber tension was adjusted to give nearly full scale reading at 260 volts. The scale is numbered in ten divisions, each one graduated to tenths and observed to hundredths. The observational uncertainty for each fiber is a little more than 0.01 division.

The voltage vs. fiber separation curve is given in Fig. 22, p. 48. It is a straight line from about 70 volts to full scale. No direct tests of the effect of room temperature on the calibration have been conducted, but the absence of anomalies, the constancy of the instrument on yearly recalibration, and the invar-quartz construction of the fiber system indicate that room temperature variations, which seldom exceed ± 5°C in this laboratory, have no effect on the instrument.

The electrostatic capacity of the electrometer is 3.80 cm. This was measured by sharing of charges between the electrometer and three cylindrical condensers whose diameter (4.87 cm.) matched the electrometer collar, and whose lengths were 20.16, 35.26 and 50.16 cm. The center axial electrodes were 0.0975 cm. in diameter and 1 cm. shorter than the outside cylinders. The top of the cylinder was fitted with a standard companion collar with amber insulator, and platinum contacts from an ionization chamber. The bottom of the cylinders was closed with a brass plate bearing a specie wax insulator for centering the axial inner electrode. The companion collar, tube, and bottom plate were connected together by soldered copper connections. The use of three standard condensers of course eliminated end effects and gave check values of the electrometer capacity measurements. Many tests were made, the maximum deviation from the mean value amounting to only 0.8%; the electrometer capacity 3.50 cm. is undoubtedly good to 0.8% and corresponds to a mean fiber separation of 7.40 divisions, or 194 volts.

The variation of electrometer capacity with fiber separation was measured by sharing of charge at five different initial voltages between the electrometer and one of the ionization chambers described in the next section. As is seen in Fig. 23, p. 51, the total variation over the full scale of the instrument is only about 2%. This constancy is explained by noticing that the largest part of the total electrometer capacity is between the piano wire connector mentioned above and the case, the actual capacity of the fibers playing only a minor role.

3. THE IONIZATION CHAMBERS

The ionization chambers, of which there are now four (two used by the Geology department), are all identical. See Fig. 24. p. 51, for details of construction. They are cylindrical condensers, the principal feature of which is a circular tray completely separating the amber insulator from the main chamber. The tray is pierced axially by a small hole through which the central electrode passes, and through which water molecules must diffuse to reach the insulation room. An annular trough in the tray contains solid dehydrating agent (magnesium perchlorate trihydrate) which absorbs any moisture reaching the insulation room. A grounded brass gauze covers the dehydrating agent trough to preclude the possibility of release of ions from it. This device has protected the insulation, not only from water wapor, but also from the various types

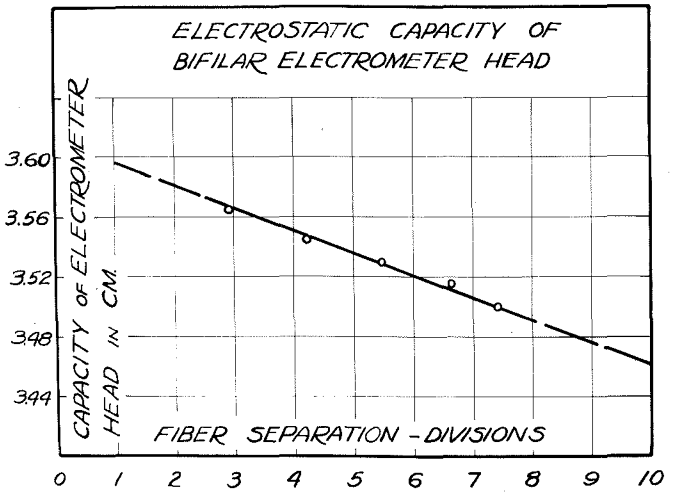

Fig. 23. Change of capacity of the electrometer with fiber separation.

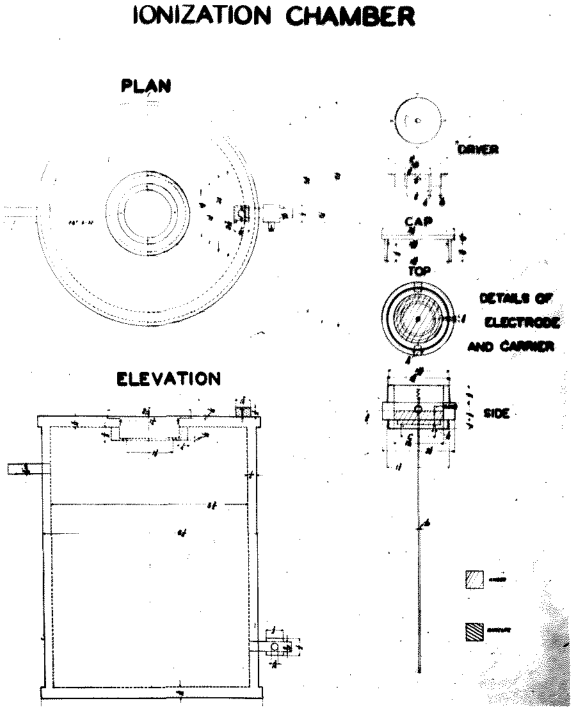

Fig. 24. Construction of the ionization chambers, showing insulation drying tray.

of heavy ions which have reached the ionization chamber from the rocks boiled in the furnace. The insulation is frequently tested and shows no increase in leakage after nearly three years of severe and varied use.

A brass guard ring buried in the bottom surface of the amber insulation and held at the original charging voltage throughout all runs reduces the potential drop across the insulation. The insulation surface is not plain but is circularly grooved to increase the surface path over which conduction takes place. The insulation leakage is about 0.002 div. per hr. (0.05 volts per hr.).

The chambers are brass cylinders of 1/4 in. wall thickness, 7.30 cm. inside radius, 19.05 cm. inside height, and with 5/16 in. top and bottom plates. The central electrode is a 0.145 cm. brass wire (0.100 cm. steel in the Geology department's chambers). A companion collar carries the amber insulator and receives the collar of the electrometer which it supports. The axial central electrode projects through the amber, where it ends in a flat platinum-faced spring which makes contact with the central electrode of the electrometer.

A brass cap covers the collar when the chamber is not in use.

4. ELECTROSTATIC CHARACTERISTICS OF THE IONIZATION CHAMBERS

a. ELECTROSTATIC CAPACITY

The electrostatic capacity of the ionization chanbers is 3.07 cm. ± 0.5%. This is determined by sharing of charges with the electrometer. Measurements of ionization currents are always made with the electrometer mounted on the ionization chamber throughout the entire run, never by the charge sharing method of Paneth and Koeck[1] which gives very inconsistent results on this apparatus, though there is little essential difference in the important constructional details of the

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1) Paneth and Koeck, Zeit. f. Ph. Chem., Bodenstein Festband, 1931.

collars and contacts.

b. GUARD RING EFFECTS

Bacause the guard ring protects only the inside surface, and does not cut down the potential drop across the main volume of the ionization chamber insulation and the electrometer insulation, there is an electrostatic soaking effect after charging the instrument. With case grounded, guard ring held at 253.5 volts, and central system (fibers and center electrode of ionization chamber) originally charged to 253.5 volts, there is a soaking effect of 0.10 divisions (2.7 volts) over a period of 20 minutes after which there is no further observable effect. This could have been largely eliminated by guard rings passing completely through both insulators.

When the system is charged, any variation in the guard ring voltage causes a redistribution of the charges on the central system, due to induction. This effect is 0.00251 divisions (0.0673 volts) per volt change in guard ring potential and is entirely linear. Because the guard ring is held at constant potential (253.5 volts) throughout all runs no corrections are necessary, but it is important to notice that the method of following the fiber voltage indication with a potentiometer adjusting the guard ring voltage, as used by Bastings$^{1)}$, is open to serious objection unless this correction is recognized and applied.

c. CHARGE SENSITIVITY

We have seen that the combined capacity of the electrometer and ionization chamber is 3.50 + 3.07 = 6.57 cm. at a mean fiber separation of 7.4 divisions, and varies less than 1% from this value between 5.4 and 9.4 divisions, where all readings are taken. Furthermore one scale

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1) Bastings, Jour. of Sci. Inst., 5, 113, (1928).

division equals 26.8 volts. A discharge of one scale division therefore indicates the passage of 0.588 e.s.u. of charge or 1.23 x 10^9 singly charged ion pairs.

d. POTENTIAL GRADIENT IN THE IONIZATION CHAMBERS

By neglecting the end effects, we can calculate the approximate distribution of potential gradient in the ionization chambers. For cylindrical condensers we have the well known equations:

$$e = \frac{V_b - V_a}{2 \log \frac{b}{a}} \quad \text{and}$$

$$\frac{dV}{dr} = - \frac{2e}{r}$$

where the letters have their conventional meaning. Combining, we obtain:

$$\frac{dV}{dr} = - \frac{V_b - V_a}{\log \frac{b}{a}} \cdot \frac{1}{r}$$

Substituting $V_b - V_a$ = 253.5 volts, b = 7.30 cm. and a = 0.0726 cm., we find the following radial and volumetric distribution of potential gradient.

r (cm)	0.0725	1	2	3	4	5	6	7	7.30
$\left(\frac{r}{7.30}\right)^2$ = fractional volume		0.019	0.075	0.17	0.30	0.47	0.67	0.92	1.00
$\frac{dV}{dr}$ $\frac{\text{volts}}{\text{cm}}$	752.	54.5	27.2	18.16	13.62	10.90	9.08	7.78	7.47

The effect of the ends will be to increase these potential gradients, but we can expect only about 90% saturation at best, as is shown on page 66.

C. ABSOLUTE CALIBRATION OF THE APPARATUS IN TERMS OF RADIUM

1. THE CURIE UNIT AND THE EQUILIBRIUM TIME

The determination of the radium content of a substance is carried out by measuring the quantity of radon associated with the radium. If equilibrium is present one curie[1)] of radon corresponds to one gram of radium. The fraction of the equilibrium amount of radon present in a sample at any time can be calculated from the known decay constant of radon. It is now necessary to determine the constant of the electrometer-ionization-chamber system, which will be expressed in curies per division per hour measured after equilibrium between the radon in the chamber and its decay products has been reached. This equilibrium is generally regarded as established three hours after the introduction of the radon into the chamber. Fig. 25, p. 56, is a typical curve made with this apparatus showing ionization current as a function of elapsed time after the introduction of the radon. The ionization current is seen to have nearly a steady value between 2 hr., 20 min. and 5 hr., 20 min.

It then falls off exponentially according to the known decay rate for radon.

2. OBSERVATIONAL TECHNIQUE

Continuous readings are always taken of ionization vs. time from the moment of introduction of the radon until 5 hours, or for weak samples until 10 or 20 hours have elapsed. An electric clock provides accurate time readings. Much information has come from these extra readings, including the important discovery of a method for measuring the thorium content of rocks.

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1) Meyer and Schweidler, Radioaktivitat, 1927, p. 275.

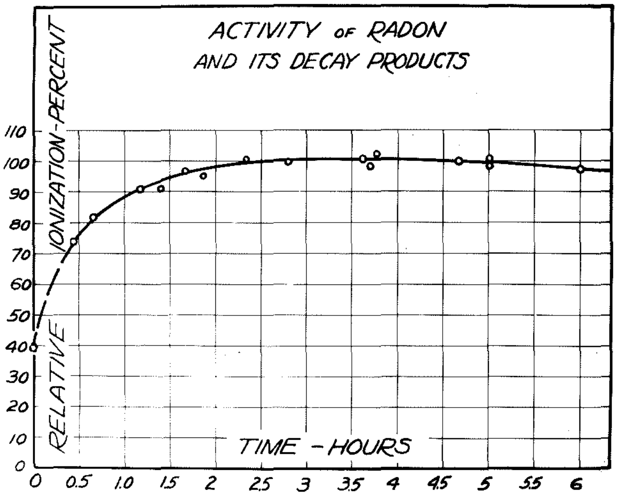

Fig. 25. Ionization current as a function of elapsed time after introducing radon into the ionization chamber.

The readings of fiber separation and time are plotted and the mean slope drawn in order to average out observational errors. Where the discharge is at a moderately high rate the most accurate readings are obtained by observing the time (to seconds) at which the fibers cross the tenths of division lines. These curves are then plotted for each fiber and the total change in fiber separation per hour is read from them. The scattering of points in these curves shows that the left fiber, which is slightly thinner, can be read more accurately than the right fiber.

For very rapid discharge rates there is time to read only one fiber. In this case the left fiber should be read. There is a slight asymmetry in the rate of movement of the fibers; the left fiber moves 1.00 division while the right fiber moves 1.12 division, the total fiber separation changing by 2.12 divisions. This ratio is constant to 1%.

For the very slow discharge rates due to ordinary rocks the fibers cross tenths of division lines only about once an hour. Therefore readings cannot be made by the method described above, but the fiber positions must be estimated to hundredths of large scale divisions about every 20 minutes and the values of fiber separation plotted against time. A straight line is drawn through these points, averaging out the observational errors, and the slope in divisions per hour is taken as the discharge rate. If the readings are taken at too short time intervals the slow motion of the fibers tricks the observer into plotting a sinuous curve. This spuriousness can be avoided by taking readings over 20 min. time intervals and for a total time of several hours.

The natural leak or "background" is observed by the method of the preceeding paragraph except that readings are extended overnight giving a total time interval of about 12 hours. Such a determination of the average background precedes every test of radioactive material. The average background varies slightly from run to run, but has never varied by more than 4% from the grand mean value. This is to be contrasted with the methods of many observers, who permit variations as large as 100%.

3. CALIBRATIONS OF THE APPARATUS AGAINST RADIUM STANDARDS

a. CALIBRATION BY STANDARD RADIUM SOLUTION

Solutions of soluble radium salts are known to be reliable standards only if they are acidic. Otherwise precipitation or adsorption of radium by the glass walls takes place and may reduce the dissolved radium even to 50% of its original value1). Hydrochloric acid is most suitable.

The standard radium solution available for the present work was kindly loaned by J. H. Ransome to McMillan2), who attributed it to the Radium Institute of Chicago and gave its radium content as 4.87×10^{-11} grams of radium per cc. The density of the solution is the same as that of distilled water as measured with a Mohr Balance at 22°C. The observational uncertainty I estimate at 0.2%. This determination allows small amounts of the solution to be weighed out instead of pipetted as has been usual heretofore, and this procedure reduced the discrepancy between successive calibrations of the electrometer to 1%, whereas when pipetting 20% deviations have been noted.

I entertain some doubt, however, about the absolute value of the solution. This is because the acidity, as measured colorimetrically

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1) Rutherford and Boltwood, Am. Jour. Sci., 20, 55, (1905); 22, 1, (1906). Eve, Am. Jour. Sci., 22, 4, (1906).

2) McMillan, M.S. Thesis, C.I.T. (1929), p. 12.

with litmus paper, is certainly below 0.01 normal, though it is also certainly acidic. The literature does not disclose whether this acidity is sufficient to retain all the radium in solution. However, the agreement of the calibrations obtained with this solution and two of the other three methods to be described indicates that the solution may be nearly correct.

By diluting 2 gm. samples of the solution in 500 cc. of distilled water, boiling in air for 20 minutes to expel all the radon, then sealing the solutions in vessels as described under the section on analysis of waters, and analyzing for radon after the elapse of known periods, a value of 34.6×10^{-12} curie per division per hour is obtained for the apparatus. The deviation between successive analyses is about 1%.

b. CALIBRATION BY CARNOTITE ORE

A sample of carnotite of unknown geological origin is also available. The material is finely powdered, and was analyzed for the Denver Fire Clay Company by Ledoux and Company of New York. Ledoux are reliable analysists of uranium, and their value of 1.59% uranium in this carnotite can be accepted as accurate.

The radium-uranium ratio for carnotites is however quite uncertain. Maurice Curie1) cites values between 2.3×10^{-7} and 3.6×10^{-7} while Lind and Whittemore2) obtained values between 2.48×10^{-7} and 4.6×10^{-7}. These deviations are explained by leaching and redeposition effects, carnotite being a secondary mineral.

Large bodies (one ton to a carload) of well mixed carnotite ore possess2) more nearly the normal radium-uranium ratio of 3.4×10^{-7}.

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1) Maurice Curie, "Le Radium et les Radio-elements", Bailliere, Paris, 1925, p. 147.

2) Lind and Whittemore, U.S. Bureau of Mines Tech. Paper 88, (1915), p. 28; Jour. Am. Chem. Soc., 36, 2066, (1914).

Small bodies of ore or isolated specimens have abnormal ratios. There is no evidence to indicate what the correct ratio for the present carnotite should be, hence 3.4×10^{-7} has been arbitrarily assumed.

Another unfortunate characteristic of carnotite is its high emanating power. The term emanating power was introduced by Boltwood1) to name the fraction of the equilibrium quantity of radon theoretically associated with the radium in a rock, which is given up to the air at room temperature. This loss of radon is between 3 and 8% for dense minerals like pitchblende but varies between 15 and 55% for carnotite. The emanating power varies from sample to sample, is a function of temperature and humidity, and will decrease markedly in carnotite if the material is heated to 400°C for half an hour2).

The emanating power of the present carnotite sample was found by McMillan3) to be 53.3%. Judging from the constancy of the quantity of radon released from this carnotite in my furnace, the emanating power has remained constant for over three years. There is but one low value to contradict this generality.

As might be expected, the emanating power of the carnotite is also a function of temperatures above 400°C. Fig. 12, p. 31, shows the dependence at elevated temperatures. These points were obtained from small specimens ranging from 0.0245 to 0.2180 gm., some heated in the bar furnace described on p. 18 and some in the furnaces described in appendices A and B, some measured with air in the ionization chamber, and some with CO_2. The fact that they fall so well on a smooth curve confirm the views that: a) k for CO_2 = 1.00 (p. 75), b) the emanating

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1) Boltwood, Phil. Mag., 9, (1905).
2) Mackay, Proc. Roy. Soc. of Canada, 15, 95, (1921).
3) McMillan, M.S. Thesis C.I.T., (1929), p. 16.

power of the cold sample is nearly constant (one clear exception), c) the emanating power is a continuous function of temperature.

The emanating power is regarded as 100% at 1600°C where all the radon is removed by the direct heating. Taking this value of the total radon in equilibrium with the radium in the carnotite, and assuming 1) a cold emanating power of 53.3%, 2) a Ra/U ratio of 3.4×10^{-7}, we obtain for the constant of the electrometer

$$36.0 \times 10^{-12} \text{ curies per division per hour.}$$

4. THEORETICAL CALIBRATIONS

a. BY THE EMPIRICAL FORMULA OF DUANE AND LABORDE

Duane(1) was the first to attempt the determination of a formula for the calibration of an ionization chamber when only its physical characteristics were known and no radium standards were available. His empirical formula, which was backed by a cursory theory, was revised by Duane and Laborde(2) who gave the current, I, in a cylindrical ionization chamber of surface, S, volume, V, walls of unstated material, and air filled as $I = 13.15\ (1 - 0.572 \frac{S}{V})$ e.s.u. per sec. per gm. sec. of radon in equilibrium with its decay products. The coefficient 13.15 becomes 6.27×10^6 when multiplied by the latest value of $\lambda^{-1} = 4.7687 \times 10^5$ to convert gm. sec. of radon to the modern unit, curies of radon.

Schmidt and Nick(3) assumed Duane and Laborde's constant 0.572 correct and found values for the first constant of 6.07×10^6 and 6.36×10^6 in two ionization chambers of diameter 7.1 cm. and height 25.2 cm., and 7.1 cm. diameter and 6.5 cm. height respectively. However

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1) Duane, Jour. dr Phy., 4, 605, (1905); C.R., (1905), 1, 581.
2) Duane and Laborde, C.R., (1910), 1, p. 1421.
3) Schmidt and Nick, Phy. Zeit., 13, 199, (1912).

the accuracy of their standard radium solution was questioned by Mache and Meyer1), who claimed it to be only 89.2% of the assumed value. Ramsey2) assumed 0.572 correct, and found Duane and Laborde 9% high for the first constant, using radon standard E 54 of the Bureau of Standards which was accurate to 3%. Gockel3) gave the first constant a value of 6.02×10^6 and assumed 0.572 correct, but offered no experimental data.

A recomputation of the few experimental data available indicates that the constant 0.572 is open to question, and may be as much as 15% high. These computations are not presented here because an entirely new equation for the effect is offered in the following section, and the constant 0.572 loses some of its significance.

Using the Duane and Laborde formula

$$I = 6.27 \times 10^6 (1 - 0.572 \frac{S}{V}) \text{ e.s.u. per sec. per curie}$$

and substituting the physical characteristics of the ionization chambers and electrometer used in the present work, a calibration constant of

$$33.2 \times 10^{-12} \text{ curie per division per hour}$$

is obtained.

b. NEW FORMULA FOR THE WALL EFFECT IN ALPHA RAY IONIZATION CHAMBERS

It is well known4) that a negatively charged wire exposed to the air collects radium A, the first decay product of radon, and Mc Gee5) and others have shown that radium D recoil atoms from radium C carry a positive charge. We may depend upon the negatively charged electrode in an ionization chamber to collect substantially all the radium A atoms and

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1) Mache and Meyer, Phy. Zeit., 13, 199, (1912).
2) Ramsey, Am. Jour. Sci., 40, 309, (1915).
3) Gockel, "Die Radioaktivetat von Boden und Quellen", Viewig 1914, p.102
4) Dadourian, Am. Jour. Sci., 19, 16, (1905).
Kovarik and McKeehan, Bull. of Nat. Res. Council, 10, No. 51, p. 140, (1925).
5) McGee, Phil. Mag., 13, 1, Jan. 1932.

hold all the successive decay products.

Duane1) has reported that if a thick center electrode, such as a wire, is used no difference in total ionization results from reversing the polarity of the chamber, thus reversing the site of decomposition of the radon decay products. However if a thin center electrode, such as an aluminum foil or the gold leaf of an electroscope is used, the ionization is as much as 12% greater if the decay products are collected on the foil than if they are collected on the ionization chamber walls. This is because a thick electrode completely absorbs any alpha particles directed into it, while a foil allows some alpha particles to pass through it and produce ionization on the other side.

In the present experimental work, as well as the following new theoretical discussion, the central wire electrode is always chosen negative, and hence collects all the decay products. Since the direction of ejection of alpha particles is entirely random, half of those due to the decay products will be absorbed in the center electrode. Most of the other half will have their entire energy absorbed by the gas in the ionization chamber, since the radius of the chamber exceeds the maximum range of the alpha particles. Each alpha emitting substance in equilibrium with 1 curie of radon ejects2) 3.7×10^{10} alpha particles per second. Each alpha particle from radium A creates 1.70×10^{5} ion pairs while each alpha particle from radium C' creates 2.20×10^{5} ion pairs. Hence the decay products in equilibrium with one curie of radon, neglecting end effects in the ionization chamber, will produce

1) $3.7 \times 10^{10} \times \frac{1}{2}(2.20 + 1.70) \times 10^{5} = 7.22 \times 10^{15}$ ion pairs per sec.

End effects will tend to decrease this value because alpha particles leaving the ends of the center electrode and directed toward the

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1) Duane, Jour. de Phy., 4, 605, (1905).
2) Rev. Mod. Ph., 3, 439, (1931).

end ~~of the~~ walls will reach them, losing some of their energy there.

It can be seen that the fractional loss depends on the height of the chamber, the distance between the bottom of the chamber and the end of the central electrode, and the type of gas in the chamber. Assume it is of the form c/h, where c is a constant for a given gas and h is the height of the chamber, then we have

2) $$7.22\ (1 - \frac{c}{h})10^{15} \text{ ion pairs per sec. per curie.}$$

The radon, however, is in the gaseous phase and uniformly distributed throughout the chamber. The range of the radon alpha particle is 4.122 cm in air, hence any alpha particle originating within 4.122 cm of the wall, and being directed toward the wall will not produce the full amount of its possible ionization of the air, some of its energy being absorbed by the wall. If the thickness of this layer is 4.122 cm. it will contain a fraction 4.122 S/V of the total number of radon atoms where S is the total wall surface in sq. cm. and V is the total volume in cc. Neglecting the effect of the curvature of the wall and of the angles at the ends of the chamber, and assuming: 1) that 1/6 of these alpha particles are directed normal to the wall, and 2) that on the average all of them have half their energy absorbed by the wall, we find that the fractional loss of ionization due to the collision of alpha particles with the wall is

3) $$\frac{4.122}{s} \times \frac{1}{6} \times \frac{1}{2} \times \frac{S}{V} = \frac{0.34}{s}\frac{S}{V}$$

where s is the stopping power of the gas used. If the neglected effect of the corners and wall curvature increases the factor 0.34/s by a, whereas the ions formed by collision of the alpha particle and the wall decrease it by b, then the fractional loss of ionization is

4) $$(\frac{0.34}{s} + a - b)\ \frac{S}{V}$$

and the whole ionization due to the alpha particles from one curie of radon will be

5) $3.7 \times 10^{10} \times 1.55 \times 10^{5} \times \left[1 - \left(\frac{0.34}{s} + a - b\right)\frac{S}{V}\right]$ ion pairs per sec. per curie,

where 1.55×10^{5} is the number1) of ion pairs formed by an alpha particle from radon, or, multiplying:

6) $5.73 \times 10^{15}(1 - m\frac{S}{V})$ ion pairs per sec. per curie, where

7) $m \equiv \frac{0.34}{s} + a - b$

and is to be experimentally determined. It can be seen that m will depend on the geometry of the ionization chamber (a), on the wall material (b), and on the stopping power (s) of the gas used in the chamber since this determines the thickness of the layer of gas sending alpha particles to the wall. Probably **(a)** is also a function of **(s)** as well as of the geometry of the chamber.

The total ionization produced in a cylindrical chamber whose radius is greater than the range of radium C' alpha particles (6.971 cm. in air) is therefore

8) $\left[7.22(1 - \frac{c}{h}) + 5.73(1 - m\,\frac{S}{V})\right] 10^{15}$ ion pairs per sec. per curie.

There are sufficient data in the literature to permit **approximate evaluation of m and** c. A less exact formula bearing on this same effect was worked out experimentally by Duane and Laborde2), superseding Duane's3) earlier formula which was clearly invalid because not dimensionally homogeneous. They gave for the current, I, due to radon and its decay products

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1) Rev. Mod. Ph., 3, 439, (1931)
2) Duane and Laborde, C.R. (1910), 1, p. 1421.
3) Duane, Jour. de Phy., 4, 605, (1905); C.R. (1905), 1, p.581.

9) $I = 6.27 \times 10^6(1 - 0.572 \frac{S}{V})$ e.s.u. per sec. per curie[1)]

as valid using air in 3 chambers whose dimensions were:

chamber	length	diameter
1	58.6 cm.	33.4 cm.
2	23.9	10.83
3	12.6	6.70

The wall material is not mentioned, but is probably zinc, since this was used by Duane in his early work.

For radon alone, without its decay products, they gave

10) $I = 2.48 \times 10^6(1 - 0.517 \frac{S}{V})$ e.s.u. per sec. per curie[1)].

This empirical formula is seen to conform to Eq. 8 when $(1 - \frac{c}{h}) = 0$, since then no decay products are effective. This indicates that $m = 0.517$ and we can now solve for c, and also the percent saturation, j, because we know that

11) $5.73\, j\, (1 - 0.517 \frac{S}{V})10^{15} \times 4.77 \times 10^{-10} = 2.48 \times 10^6(1 - .517\frac{S}{V})$.

This gives j = 90.7 %, say 90%, value in fair agreement with the known percent saturation values[2)] for alpha particles and the known potential gradient in the present ionization chamber (see p. 54). Substituting in formula 8) and multiplying by $4.77 \times 10^{-10} \times .90$ to transform the number of ions formed into the e.s.u. actually collected, we obtain

12) $\left[3.10(1 - \frac{c}{h}) + 2.46(1 - .517 \frac{S}{V})\right] 10^6$ e.s.u. per sec. per curie.

Substituting the dimensions of the ionization chambers used and assuming a value of 35.0×10^{-12} curies per division per hour as the true calibration of the instrument we find c = 2.5 cm. Then for the loss of ionization from the decay products on the central electrode due to some of their alpha particles striking the upper and lower ends of the ioniza-

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1) The coefficients of Duane and Laborde were for gm. seconds of radon, a unit no longer in use. I have converted these to curies by multiplying by $\lambda^{-1} = 4.7687 \times 10^5$ for radon.

2) Meyer and Schweidler, Radioaktivitat, (1927), p. 281.
Broessler, Akad. Wess. Wien. Ber. 129, 2a, 47, (1920).

tion chamber we obtain the value $\frac{c}{h} = \frac{2.5}{19.05} = 13\%$. This is a reasonable value.

The theoretical value of the constant, c, can be estimated as follows. Assume the decay products are uniformly distributed along a central electrode which extends the entire length of the ionization chamber, h. Then the fraction of the radium A molecules which are within an alpha track length of the ends is $\frac{2 \times 4.722}{h}$, and as before we may assume 1/6 of these are directed normal to their adjacent end wall. On the average all of these particles will lose half their ionizing energy by collision with the wall, that is 1/2 of 2.20×10^5 ion pairs per alpha particle. Similarly the fractional loss of radium C' ionization will be $\frac{2 \times 6.97}{h} \times \frac{1}{6} \times \frac{1}{2}$ of 1.70×10^5 ion pairs per alpha particle. The fraction of the total ionization due to radium A and radium C', remembering that half of it has already been assumed lost in the central electrode is therefore:

$$\frac{3.7 \times 10^{10} \times \frac{1}{6} \times \frac{1}{2}\left(\frac{2 \times 4.722}{h} \times 2.20 + \frac{2 \times 6.97}{h} \times 1.70\right)10^5}{\frac{3.7 \times 10^{10}}{2}\,(2.20 + 1.70)10^5} = \frac{1.90}{h}$$

Thus c is found to be approximately 1.90 cm. Considering the simplifying assumptions made in this derivation, and the absence of sufficient reliable experimental data I consider this a sufficiently close check to suggest the validity of Eq. 8 and the theory described above. The apparatus for a thorough precision determination of c and m, the constants of Eq. 8, in several gases has been designed and the measurements should be completed early in the coming summer.

c. CALIBRATION BY THE NEW THEORETICAL FORMULA

If we take the theoretical value 1.90 cm. derived in the last section for c, and apply Eq. 12 to the present apparatus, we find:

$$I = 4.76 \times 10^{6} \text{ e.s.u. per sec. per curie}$$

or

$$C = 34.4 \times 10^{-12} \text{ curies per div. per hour.}$$

Because the readings are begun about 3 hours after introducing the radon in the ionization chamber, this value must be divided by 0.975 the fraction of the original radon remaining at that time. This gives

$$C = 35.2 \times 10^{-12} \text{ curies per div. per hour}$$

as the theoretical calibration of the instrument.

d. SUMMARY OF CALIBRATIONS

Four evaluations of the calibration constant of the present electrometer-ionization chamber system have been described. These are:

1) $C = 34.6 \times 10^{-12}$ by the standard radium solution
2) $C = 36.0 \times 10^{-12}$ by the standard carnotite ore
3) $C = 33.2 \times 10^{-12}$ by the empirical formula of Duane and Laborde
4) $C = 35.2 \times 10^{-12}$ by the new theoretical formula of Eq.8 or 12, derived in the preceeding section,

where the units are curies per div. per hr. in all cases.

The separate ground for questioning each of these values have been presented in the sections dealing with each method.

The true calibration constant assumed for the present analyses will be

$$C = 35. \times 10^{-12} \text{ curies per div. per hour}$$

where the discharge rate is measured from 3 to 5 hours after introducing the radon into the apparatus and the curies are those originally present.

e. SATURATION CURRENT

As already shown the potential gradient in the ionization chamber collects only about 90% of the ions formed. It is to be expected that the absolute or radium calibration of the system will vary with the voltage on the ionization chamber, or, what is the same thing, with the scale reading of the electrometer. Fig. 27, p. 70, shows the experimentally determined variation of the sensitivity of the system as a function of fiber separation. This curve represents 35 observations; the mean deviation from the average curve shown is about 0.8%. The curve is the same, within the observational uncertainty, for the background and for alpha ray ionization in both air and CO_2. All radium determinations are corrected for this effect, a fiber separation of 7.4 divisions being arbitrarily taken as the standard of reference.

f. EFFECT OF VARYING TEMPERATURE AND PRESSURE

Bragg1) and Lepape2) have shown that for ordinary laboratory temperatures there is no change in observed alpha ray ionization with temperature.

The ionization chambers are always operated at pressures between 740 and 750 mm. The careful investigations of Ludewig and Lorenser3), Lepape2), Lester4), Mader5), and others have shown that for these limits of pressure variation, the variation in total ionization is certainly less than 0.5%.

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1) Bragg, "Studies in Radioactivity", Macmillan (1912), p. 59.
2) Lepape, C.R., 176, 1613, (1923).
3) Ludewig and Lorenser, Zeit. f. Ph., 13, 284, (1923); 21, 258, (1921).
4) Lester, Am. Jour. Sci., 44, 225, (1917); J.O.S.A., 11, 637, (1925).
5) Mader, Phys. Zeit., 33, 178, Feb. 15, 1932.

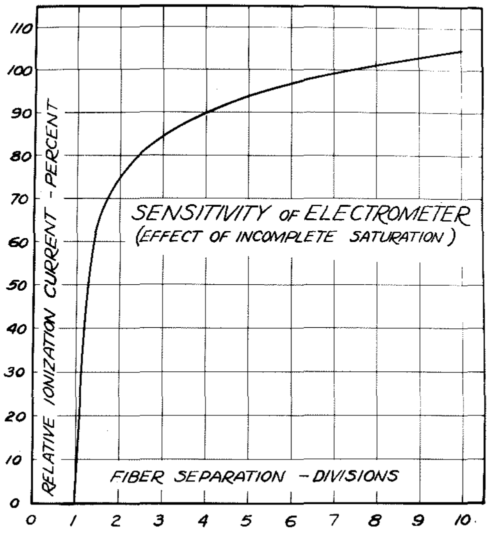

Fig. 27. Variation of the sensitivity of the electrometer, plotted as a function of fiber separation. This effect is wholly due to incomplete saturation since the capacity variation, Fig. 23, is very small and oppositely directed.

Accordingly, no corrections for ionization chamber temperature and pressure are required.

D. USE OF CO_2 IN THE IONIZATION CHAMBERS

1. ADVANTAGES, STOPPING POWER, MOLECULAR IONIZATION AND SPECIFIC IONIZATION

Carbon dioxide from tanks more than one month old is used in the ionization chambers because it provides a reproducible, dry, radon and thoron free background gas. In order to compare measurements of radon in which the ionization chamber is air filled, with measurements using a CO_2 filling, we must know the ionization produced in CO_2 by the alpha rays from radon, radium A and radium C' relative to the ionization by the same particles in air.

Experiments closely related to this problem have been carried out by many investigators. Two fundamental principles are involved. The relative stopping power of any substance is the ratio of the retardation suffered by an alpha particle in passing through a given thickness of the substance, to the retardation experienced in the same thickness of air at standard conditions. Bragg1), Kleeman2), and others3) have shown experimentally that the stopping power of an atom is approximately proportional to the square root of its atomic weight. Taylor4), Bates5), Gibson and Eyring6), and others7) have shown that the relative stopping power also depends on the velocity of the alpha particle.

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1) Bragg, "Studies in Radioactivity", p. 64. Macmillan, (1912). Phil. Mag., (1906), 1, 620; (1907), 1, 333.
2) Kleeman, Proc. Roy. Soc., 79, 220, (1909).
3) Rutheford, Chadwick and Ellis, "Radiations from Radioactive Substances" p. 97.
4) Taylor, Phil. Mag., 26, 402, (1913).
5) Bates, Proc. Roy. Soc., A, 106, 622, (1924).
6) Gibson and Eyring, Phy. Rev., 30, 553, (1927).
7) Rutheford, Chadwick and Ellis, loc. cit.

We are here concerned only with the specific ionization, or relative total ionization due to alpha particles from radon, radium A, and radium C', in CO_2 and air. The specific ionization, k, is the ratio of the molecular ionization to the stopping power.

2. SPECIFIC IONIZATION OF CO_2

The values for the specific ionization of CO_2 relative to air obtained by various observers using many different types of ionization chambers are shown in the following table.

Observer	k	Alpha Particle Source	Collecting voltage
Rutheford[1]	0.96	U	800
Laby[2]	1.03	U	400
Bragg[3]	1.08	RaC'	1000 per cm
Kleeman[4]	1.08	RaC'	1000 per cm
Bragg[5]	1.03	RaC'	1000 per cm
Taylor[6]	1.01	Po	200 per cm
Hess and Hornyak[7]	1.25	Po	0 to 3500 per cm
Lepape[8]	0.90	Rn, RaA, RaC'	300
Gibson and Eyring[9]	0.996	Po	200
Diebner[10]	1.01	Po	600 per cm
Mader[11]	1.01	Po	0 to 1000
Evans	1.04	Rn, RaA, RaC'	250

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1) Rutheford, Phil. Mag., 47, 136, (1899).
2) Laby, Proc. Roy. Soc., 79, 206, (1907).
3) Bragg, Phil. Mag., 13, 333, (1907).
4) Kleeman, Proc. Roy. Soc., 79, 220, (1907).
5) Bragg, "Studies in Radioactivity", Macmillan, (1912), p. 64.
6) Taylor, Phil. Mag., 21, 571, (1911).
7) Hess and Hornyak, Akad. Wiss. Wien. Ber., 129, 2A, No.7, 661, (1920)
8) Lepape, C. R., 176, 1613, (1923).
9) Gibson and Eyring, Ph. Rev., 30, 553, (1927).
10) Diebner, Ann. d. Physik, 10, 8, 947, (1931).
11) Mader, Phy. Zeit., 33, 178, Feb. 15, 1932.

Hess and Hornyak regarded the results of Taylor as the most reliable work then done, and explained their own high results as due to realization of complete saturation.

The decreased total ionization observed in an ionization chamber due to the impact of alpha particles with the walls was discussed on p. 64. The thickness of the layer of gas affected by the walls depends on the stopping power of the gas. Increasing the stopping power of the gas decreases the thickness of this layer, reducing the number of alpha particles which reach the wall. Thus the ionization defect factor, m, of Eq. 8, p. 65, is decreased, and the total ionization in the chamber should be greater in CO_2 than in air. This conclusion is in agreement with the experimental results to be described in the next paragraph, but is at variance with the experimental results of Lepape[1] who found that the relative total ionization produced by radon and its decay products in a cylindrical ionization chamber of 3140 cc. volume, (12 cm. inside diam., and 27.5 cm. height, with central electrode 0.8 cm. in diam.) varied with the mol percent of CO_2 in air as follows:

mol % CO_2	k
0	1.00
9.55	0.98
15.95	0.965
32.8	0.945
63.7	0.93
92.	0.91

An accuracy of 1% is claimed for the results; but no remark on the method of obtaining a known constant source of radon nor the electrical

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[1] Lepape, C. R. 176, 1613, (1923).

polarity of the electrodes - which determines the site of decay product deposition - is made. A collecting voltage of 300 volts was used.

On the other hand, two experiments on my apparatus have indicated a value nearer 1.04 for k. These were conducted in the following way. About 0.07 gm. of carnotite was boiled in the furnace and the radon liberated led simultaneously to both ionization chambers, which were open to the furnace and themselves through about 3 feet of 4 mm. glass tubing and 2 stopcocks of 2 mm. bore, during the furnace run and for exactly 5 minutes thereafter. One chamber was then filled from 12 mm. to 750 mm. with CO_2, the other with air. This was expected to produce equal quantities of radon in the two identical chambers. However, as shown below, the discharge rates taken after three hours showed an asymmetric distribution of the radon, due to the fact that the branch lines from the furnace to the two chambers differed by about one foot in length, and that the diffusion of radon between the chambers during the extra 5 min. period when they were connected together was so low as to fail to distribute the radon equally between them. Two runs were made, the CO_2 and air being put into opposite chambers in the second run to check the symmetry of radon distribution. If x represents the fraction of radon in chamber No. 1 in the two tests, and the asymmetry of distribution is assumed constant in the 2 runs (which were identical in all respects), and if k_a, k_b, represent the apparent values observed for the specific ionization, k, then for the first run where CO_2 was in chamber No. 1:

$$k \frac{x}{1 - x} = k_a$$

and for the second run where air was in chamber No. 1:

$$k \frac{x - 1}{x} = k_b$$

solving for k, we find

$$k = \sqrt{k_a k_b} \ .$$

Substituting the observed k_a and k_b, each good to 0.4%, we get

$$k = \sqrt{1.257 \times 0.853} = 1.037 \text{ say } 1.04 \ .$$

Considering the asymmetry of distribution ($x = 0.567$) this result may be questioned with say 5%.

A method for insuring equal distribution of radon between the two chambers is being worked out, and the results obtained will be reported in the literature.

For the present work, a value of $k = 1.00$ is assumed as a fair average of all the above reports and the results are quoted as within 5%, since this limitation is imposed by other conditions mentioned in the next paragraph.

E. LIMITS OF PRECISION WITH THE BIFILAR ELECTROMETER

The observational uncertainty in the rate of discharge of the electrometer, when the rate is low and readings are taken every 20 minutes for three to five hours, amounts to about 0.008 div. per hr. For rocks of low activity this is equivalent to about 5 to 8% uncertainty in the radium content. Theoretically, the probable deviation in the background amounts to 1 to 2% for this time interval as shown on p. 41 , and similarly the probable deviation in the observed activity is of the same magnitude. It follows that this electrometer is incapable of going all the way to the natural observation limit.

F. A NEW APPARATUS FOR REACHING THE NATURAL OBSERVATION LIMIT

To reach the natural observation limit a new hook-up has been devised. The circuit is common in some branches of physics, but to the writer's knowledge has never been applied to the measurement of small quantities of radon and thoron.

Two identical ionization chambers are connected to a string electrometer so that only the difference between the ionization in the two chambers is measured. Both chambers contain identical background gases, and one also contains the radon or thoron to be measured. The electrometer readings then represent only the radioactive ionization plus the very small difference in the backgrounds due to the presence of long lived solid decay products from former runs. The string electrometer is operated at a sensitivity of about 30 divisions per volt, where it is relatively stable. This is sufficient to reduce the observational uncertainty to a value well below the statistical variations of the background and the radon or thoron being determined, measurements can then be extended to the natural observation limit, defined on p.42.

The use of two ionization chambers has four advantages and one disadvantage. It eliminates background fluctuations due to occasional penetrating x-radiation or the movement of radioactive material in the vicinity of the apparatus; it permits the use of the whole scale of the electrometer to measure change in charge, and offers greater charge sensitivity; it permits the use of higher collecting voltages; and by induction it eliminates errors due to variations in battery voltage. Its disadvantage is that the statistical variations of the background are slightly increased.

Professor Bateman, in a private communication, has extended his early analysis[1] of the statistical variations from one ionizing substance in one ionization chamber to the present case of the fluctuations observed from one ionizing material in one chamber instrumentally deducted from the combined fluctuations due to two or more ionizing agents (background and radon) in a second chamber. He has shown that

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[1] Bateman, Phil. Mag., 20, 704, (1910).

in all cases the net mean error or variation to be expected equals the square root of the total number of ionizing particles active in both chambers during the time interval employed. This is entirely analogous to the simpler case for a single chamber and indicates that the statistical variation of the background in the double-chamber system will be $\sqrt{2}$ or 1.414 times the variation for a single chamber. This is a small price to pay for the 80 fold increase in sensitivity of the string over the bifilar electrometer.

Two circuits employing the string electrometer are shown. That in Fig. 28, p. 78, involves the measurement of only a low voltage above ground. All high potentials applied to the instrument are held at their proper values by the batteries, hence errors due to insulation leakage and soaking are much smaller than in the circuit of Fig. 29, p. 78, which requires the measurement of small changes in the two voltages applied to the plates of the string electrometer. The first circuit is the steadier and more reliable one.

Data are not yet sufficiently numerous to permit precision analysis of the background variations, but five runs have indicated they are of the order of 6% per hour.

Fig. 30, p. 79, is a photograph of the apparatus showing the string electrometer between the two ionization chambers. The interconnections and platinum tipped switches are in the bridge-like square brass box joining the tops of the instruments.

G. DETERMINATION OF THORIUM

It has been found possible to determine the thorium content of rocks with this apparatus. For this purpose the furnace and ionization chamber are filled with CO_2 and this gas is circulated in a

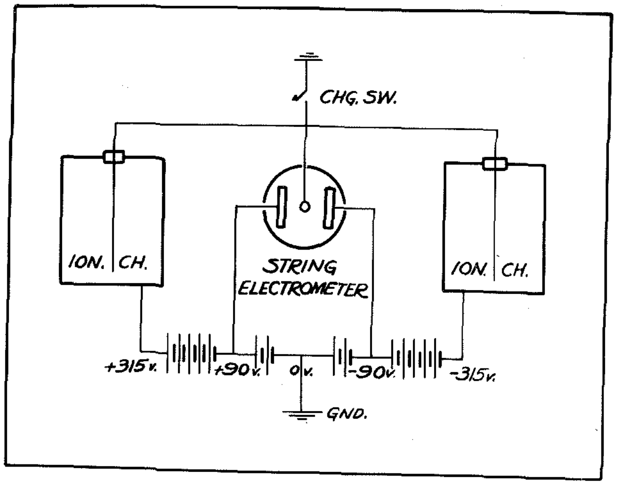

Fig. 28. Circuit diagram for high sensitivity, double ionization chamber method.

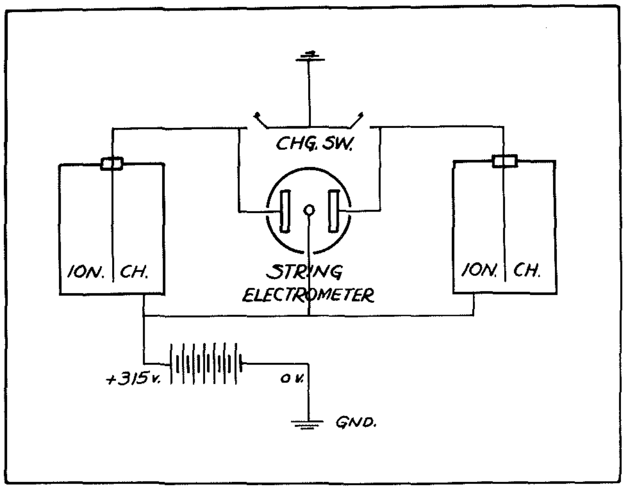

Fig. 29. Alternate circuit for double ionization chamber method.

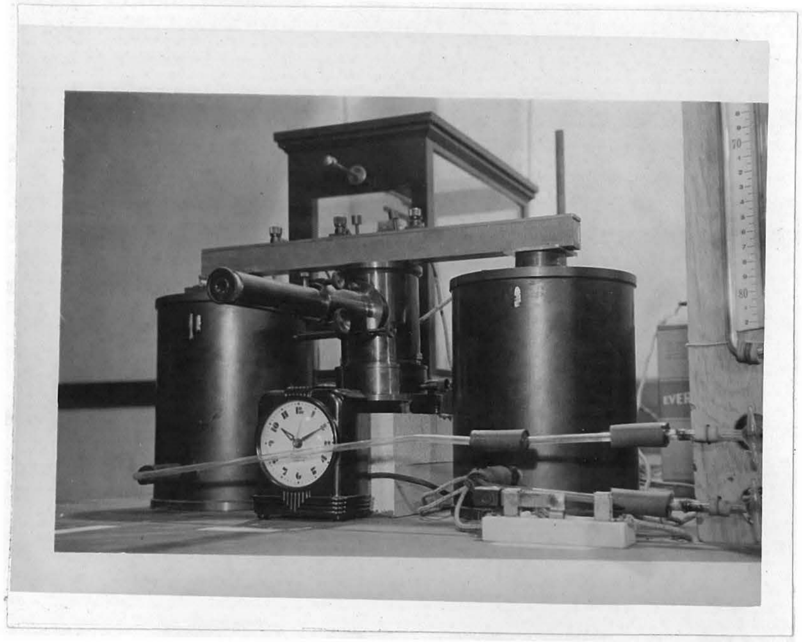

Fig. 30. String electrometer and double ionization chamber apparatus.

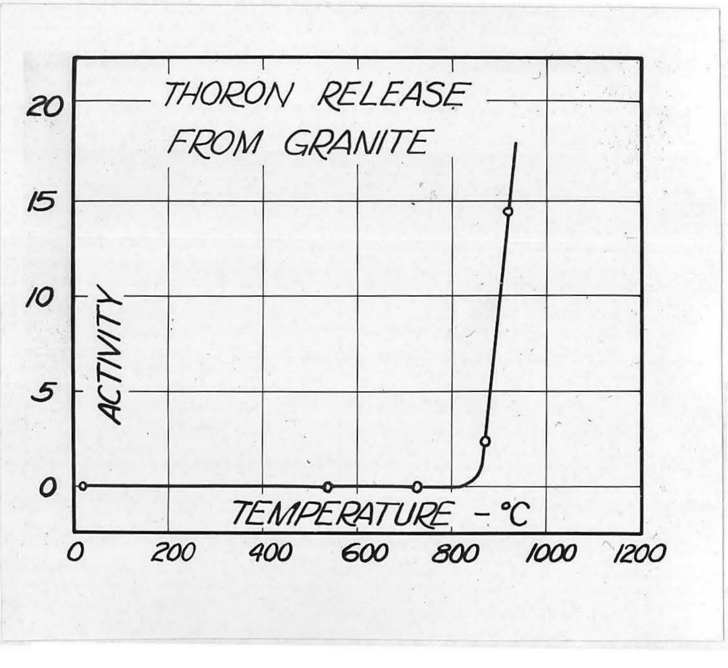

Fig. 31. Release of thoron from granite, showing 850°C threshold temperature.

~~in~~ ~~a~~ closed circuit including the furnace, ion trap, ionization chamber and circulating pump, while the rock is being boiled in the furnace. In this way the thoron produced by the thorium in the rock is removed and quickly delivered to the ionization chamber where it is measured. Because the gas system is a closed circuit, the radon liberated from the rock is conserved and it is measured in the usual way about three hours after the furnace is shut down. It is therefore possible to measure both the thorium and radium content of the same rock sample in a single run.

Because thoron has a half life of only 54.5 sec., and its longest lived decay product, thorium B, emits only beta rays, the ionization effects due to the thoron completely disappear within a few minutes. Thus the ionization due to thoron is easily resolved from that due to radon.

Thoron, like radon, is adsorbed by rubber, but for preliminary tests of this method a rubber bulb gas circulating pump was used, as this was readily available. With a gas circulation rate of 30 cc. per sec. the ionization due to thoron could be readily measured. It was found that no thoron was released from the heated rocks until a temperature of 850°C was reached, where the release began sharply. The curve was only taken to 920° and had not reached a maximum, as is to be expected by analogy with the case of radon. Fig. 31, p. 79, presents these data on the threshold temperature for thoron.

The high ionization observed during runs conducted as described just above is attributed to thoron, and not to spurious effects, such as ions from the melt, because: 1) no heavy ions have ever been observed from the furnace at or below 1020°C, 2) the gas in question passes through the electrostatic ion trap, which stops all ions (Fig. 10, p. 28), 3) the decay curve, when pumping is stopped, corresponds to the known half life of thoron.

Accurate determination of the thorium content of rocks and the temperature-percent thoron release curve await the construction of an all metal, motor-driven circulating pump of the reciprocating type, employing copper bellows and ball check valves. This is a prerequisite to reliable measurements because the electrometer calibration is a sensitive function of the gas circulation rate. Enough work has been completed to demonstrate the effectiveness of this combination analysis of both thorium and radium, and to indicate the gas circulation rates and furnace temperatures required.

APPENDIX

A. VERTICAL TUBE FURNACE

The first furnace built for this investigation was a vertical split-tube graphite resistance furnace, whose closest progenitor is perhaps the spiral tube furnace due to Arsem[1]. Scale drawings of the furnace are seen in Fig. 32, p.83, while photographs are shown in Figs. 33 and 34, p. 84. The case is of chromium plated steel 7 in. in diameter, and stands about 1/4 in. under the surface of cooling water in a larger steel vessel. The cover plate is bolted to the case and is made vacuum tight by a groove and lead-wire gasket. The cover plate carries four fiber insulated packing glands through which pass the copper tubes which carry cooling water and electric current into the hollow copper electrodes. These electrodes form the two halves of a split circle and are drawn together by bolts, clamping between themselves the graphite resistor.

The principal novelty of this furnace is the form of the graphite resistor and the copper electrodes. These are shown in Figs. 32, p. 83, and 34, p. 84. The resistor is an Acheson graphite tube split along a diameter for all but the last (bottom) inch of its length. The upper split end is reinforced by lavite insulators and firmly clamped between the copper electrodes described above. The electric current enters through one electrode, passes downward in one side of the split tube, across the intact lower end of the tube and up and out through the other side of the tube. This construction completely eliminates any danger of resistor fracture due to the thermal expansion of the graphite in ordinary rigid electrodes, for the lower end of the resistor is

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1) Arsem, Jour. Am. Chem. Soc., 28, 921, (1906).

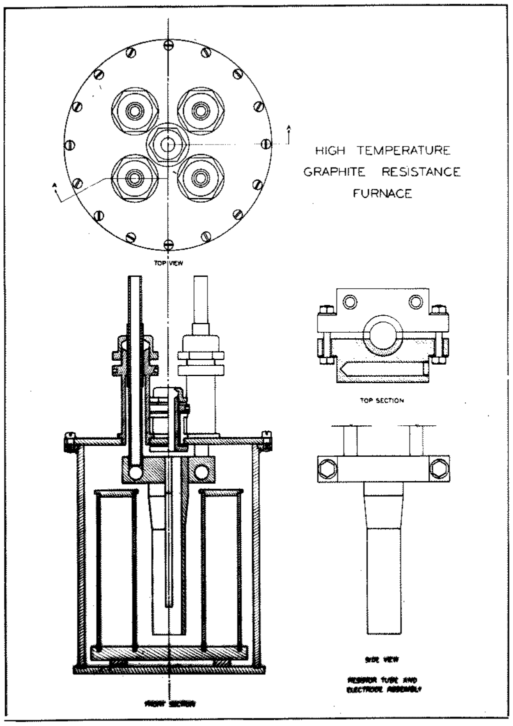

Fig. 32. Vertical split-tube furnace.

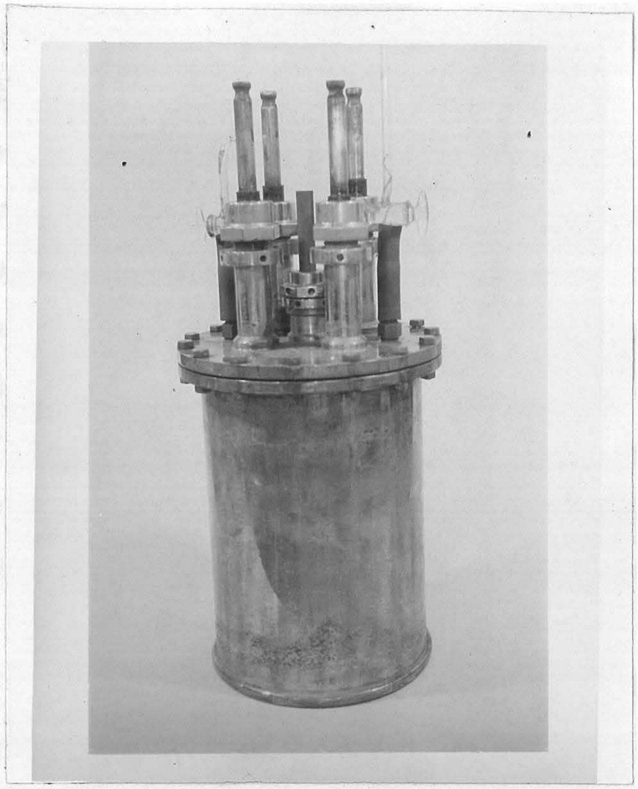

Fig. 33. Tube furnace assembled. A graphite crucible is seen in the axial stuffing gland.

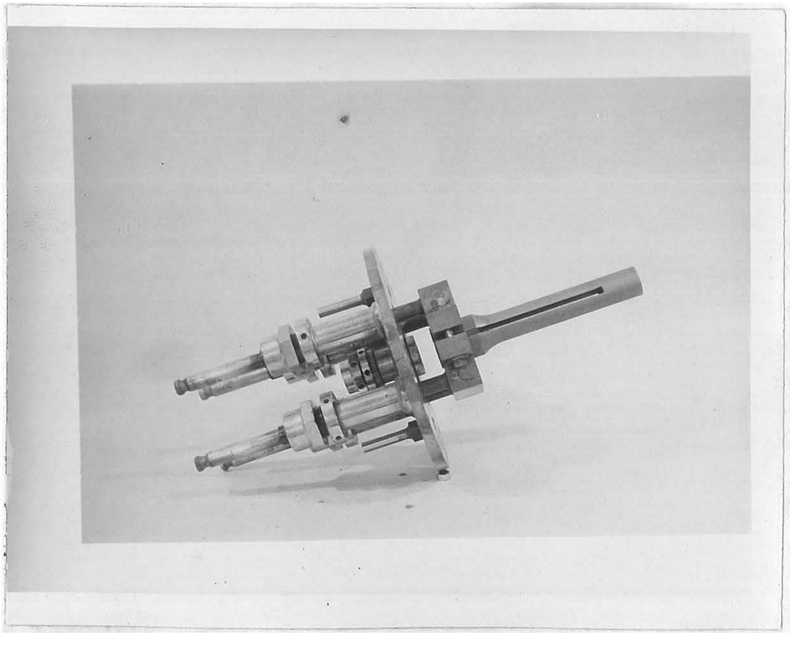

Fig. 34. Detail of furnace cover, electrodes, and split-tube resistor.

perfectly free to expand. A second advantage of this construction is that only one end (upper) of the resistor loses heat through cooling by conduction to the water cooled electrodes.

A hollow graphite radiation screen (Fig. 32, p.83) filled with graphite powder surrounds the electrode and retards heat transmission from the resistor to the cold metal walls of the furnace case.

The crucible (Fig. 33, p.84) is introduced through a 1/2 in. packing gland in the furnace cover, and extends along the axis of the resistor to the highest temperature zone. This construction permits exchanging crucibles without opening the furnace. The resistance of the split tube resistor is 0.024 ohms when new, and gradually increases to about 0.048 ohms before failure. The average resistor life when the furnace is not evacuated is 3 hrs., representing about 20 heatings and coolings. The furnace can be operated without evacuating because the graphite resistor soon burns up all the oxygen in the furnace volume and thereafter no air enters the furnace, hence inert gases only are present. Evacuation, however, lengthens the life of the resistor.

Furnace temperatures up to 1100°C were measured by a chromel-alumel thermocouple in a quartz crucible. From 900 to 2000°C a Leeds and Northrup optical pyrometer was used, temperature observations of the inside wall of the resistor being made through the 1/2 in. crucible gland in the furnace cover. Characteristic curves, showing 1) equilibrium temperature against watts input, and 2) temperature-time curves for both heating and cooling are given in Figs. 35 and 36, p. 86. As will be seen, the furnace attains 2000°C on only 7 K.W. power input.

The power supply and power control described in the main body of the thesis is used on this furnace.

When investigations of the release of radon revealed that temperatures of 1000°C did not affect complete removal, as had been

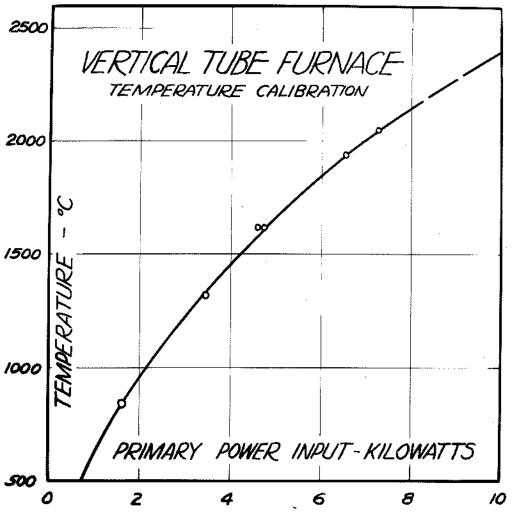

Fig. 35. Temperature calibration of vertical furnace.

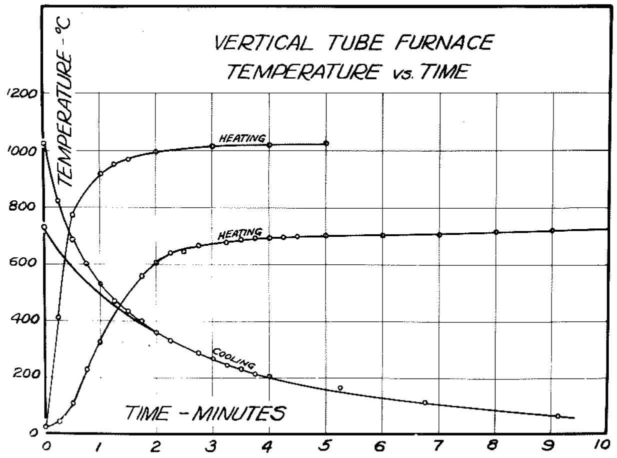

Fig. 36. Heating and cooling curves for vertical furnace.

indicated by the report of Fletcher[1], the usefulness of quartz crucibles was ended. Graphite crucibles were then used but were found to be so porous as to allow radon to diffuse out through the hot crucible walls even when dry air was being passed into the crucible through its wall in an effort to eliminate this radon loss. Neither the Acheson research laboratories, nor any other commercial source was found which could provide a gas tight, high temperature crucible. For this reason a new furnace was required which contained no crucible as such, whose volume was so small that radon could be allowed in the whole furnace volume, whose walls were cold and vacuum tight, and which also had a larger volumetric capacity for rock samples. All these requirements are adequately met by the bar furnaces described herein.

While this furnace has been superseded by the bar furnaces in this radioactive investigation, it possesses many remarkable qualities, and should be of great value in the chemical and metallurgical fields now served exclusively by the Arsem furnace.

B. SMALL BAR FURNACE

This furnace (see Fig. 37, p. 88) was built to test the practibility of the design of the large bar furnace described on pp. 18 to 25. The electrodes are essentially identical with those described for the large bar furnace. They are mounted on a circular steel plate 1 in. thick and 12 in. in diameter. The inside edges of the electrodes are spaced 3 in. apart, and a resistor 1 in. wide and 1/8 in. thick is ordinarily used. The cover of this furnace is a 7 in. diameter glass bell jar. This is cooled by water flowing over the outside surface of the glass onto the base plate, where it collects in the annular space between the bell jar walls and a 1 in. high sheet iron wall at the

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[1] **Fletcher, Phil. Mag., 26, 674, (1913).**

Fig. 37. Glass covered bar furnace.

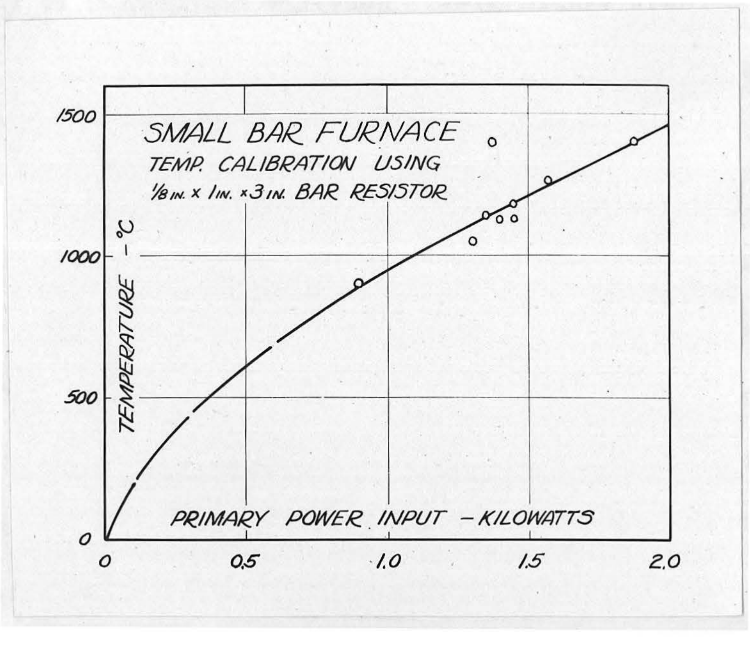

Fig. 38. Temperature calibration for bar furnace shown in Fig. 37.

perimeter of the base plate, and is then drawn off to the sink. The same power supply and control is used for this furnace. Temperature-power calibration curves made with an optical pyrometer are shown in Fig. 38. p. 88.

The great advantage of this furnace is its glass cover which permits direct observation of the heating of materials placed in it.

The proper electrode clamp pressures to just allow gliding of the resistor and prevent buckling were determined with this furnace.

C. OUTGASSING FURNACE

Powdered shales, when heated in the large furnace, frequently cause explosions, probably due to their content of organic or reactive inorganic material. Such samples, after grinding and weighing, must be roasted in an auxiliary furnace to remove these explosive materials. They are then stored for about a month to accumulate their equilibrium quantity of radon, and analyzed like ordinary granite samples.

The furnace for this purpose is 16 ft. of 20 gauge Chromel "A" wound in two layers seperated by alundum cement on a grooved alundum tube 2 in. in diameter and 5 in. long. It is mounted vertically in Sil-o-cell powder in a sheet metal cylindrical container 6 in. in diameter and 9 in. high. An alundum crucible, containing the material to be roasted, is suspended inside the tube in a chromel wire cradle. The furnace is operated on 110 volts A.C. using a series resistance. It reaches 950°C in 40 minutes at 5.2 amperes. If desired, more than 50 gms. of material can be outgassed at once.

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