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Reprinted from The Review of Scientific Instruments, Vol. 37, No. 5, pp. 614–619, May 1966

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Printed in U. S. A.

High Temperature-High Pressure Cell for Measuring Densities of Metals by Radiation Counting Technique*

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(Received 25 August 1965; and in final form, 7 January 1966)

Equipment and techniques have been developed for measurement of densities of metals at high temperatures (up to 2200°K). The equipment and techniques were demonstrated using alkali metals but are generally applicable not only to most metals but also to many other substances. Determination of vapor and liquid densities of alkali metals at high temperatures and pressures was accomplished by measuring the radiation emanating from the vapor and liquid phases of a radioactive alkali metal contained in a high pressure cell fabricated from a molybdenum-30 wt.% tungsten alloy. The procedure was used to obtain vapor and liquid phase densities of the alkali metals at temperatures up to 2200°K and pressures up to 500 atm, which approach critical conditions. The radiation counting method involves sealing the metal whose density is to be measured in a containment capsule, irradiating the capsule and metal to produce a gamma emitting isotope of the metal, charging the capsule into the high temperature cell, and counting the activity of the vapor phase and the liquid phase at temperatures ranging from room temperature up to the critical point. A calibration of density vs irradiation level is performed at low temperatures where accurate liquid density data are available.

INTRODUCTION

THE advent of space and nuclear power programs has resulted in a great interest in high temperature properties of materials, particularly those of metals. Up to the present time, no convenient technique has been available for accurate measurement of densities at temperatures above 1500°K. Alkali metals are of particular interest to space programs because of their desirable properties for many uses such as ion engine fuels and turbine fluids. The physical and chemical properties of alkali metals make them attractive for use as nuclear reactor coolants. Equipment and techniques for making high temperature density measurements on metals or other materials has been demonstrated in this study by making such measurements on the alkali metals, cesium, rubidium, sodium, and potassium.

Densities below 1500°K are usually measured by pycnometer or dilatometer techniques.[1] Both methods involve weighing an accurately known volume. However, these techniques are accurate only at temperatures well below the boiling point of the material whose density is being measured. As the boiling point is approached, boiling and evaporation begin to occur and meaningful density measurements cannot be obtained. A technique previously used for determination of the densities of mercury liquid and vapor at temperatures up to the critical point employs

* Work performed at Argonne National Laboratory, operated by the University of Chicago under the auspices of the U. S. Atomic Energy Commission, Contract No. W-31-109-eng-38. Based on Ph.D. thesis of I. G. Dillon, Illinois Institute of Technology (1965).

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[1] F. Tepper, A. Murchison, J. Zelenak, and F. Roelich, "Thermophysical Properties of Rubidium and Cesium," MSA Research Corporation Rept. No. MSAR-63-116 (Callery, Pennsylvania, February 1963).

measurements of electrical conductivity.[2] This method requires elaborate apparatus and is difficult experimentally. However, it has been used recently in work of Hochman and Bonilla[3] for determinations of density of some alkali metals as discussed below.

Basically, the method of density measurement used in this study involves activating the metal by irradiation in a thermal neutron flux to produce a radioactive isotope emitting a gamma ray suitable for counting. The metal must be contained by a material which has sufficient strength and corrosion resistance to the metal at the high temperatures involved in the measurements. The critical temperature and critical density of the metal may be then determined by measuring the densities of the vapor and liquid phases by counting the gamma activity emanating from known volumes of the irradiated metal. The critical temperature and critical density are then obtained from appropriate plots of the density data which cover the range from room temperature to the critical point. These techniques were applied to obtain the critical temperature and critical density of the alkali metals, cesium, rubidium, sodium, and potassium. If a suitable radioactive isotope of the metal whose density is to be measured does not exist, an attenuation method might be used. This would involve directing a collimated beam of radiation from a radioactive source through the metal and measuring the attenuation.

Measurement of properties at these high temperatures (up to 2200°K) and high pressures (up to 500 atm) requires special materials and techniques. Since at elevated temperatures refractory metal containers oxidize readily, it is necessary to provide a very pure inert atmosphere or to operate under high vacuum. The latter technique was used in these studies, since it was desirable to remove continually gas released by the insulation. A 76 cm diam×152 cm high vacuum tank was used as the containment vessel. A combination of a roughing pump and a diffusion pump maintained a vacuum of about 1 μ absolute pressure. In order to obtain the high temperatures required, the work piece was insulated with powdered tungsten carbide. The insulation was contained in a ceramic crucible. The alkali metal itself was contained in a thin wall capsule which in turn was contained in a massive refractory metal cylinder to provide both shielding from radiation and support against the high pressure forces within the capsule. The massive refractory metal cylinder has stepped diameter holes (simulating tapered holes which reduce scatter of radiation) leading from the vapor and liquid phase regions of the capsule wall toward the outside of the vacuum tank to the single channel analyzer which counted the collimated gamma radiation beams from the alkali metal.

DESCRIPTION OF EQUIPMENT

The alkali metal was usually contained in a molybdenum-30 wt.% tungsten capsule 3.81 cm long×0.64 cm o.d. (Fig. 1). Other materials such as molybdenum, tungsten, or molybdenum alloys were also used. These materials of construction were chosen for three reasons:

(1) Data from several sources[4–8] indicated molybdenum and tungsten had excellent corrosion resistance to alkali metals;

(2) this alloy has good high temperature strength; and

(3) neutron irradiation produced short lived radioisotopes of the container materials which would decay rapidly and not interfere with counting of the alkali metal whose density was being measured.

These same considerations would apply when selecting materials of construction for density measurements on other materials. The capsules were charged using the capsule charging assembly shown in Fig. 2. Prior to charging the capsule the alkali metals were contained in glass ampoules sealed under inert gas or vacuum. Charging was carried out in a high purity helium atmosphere glovebox.

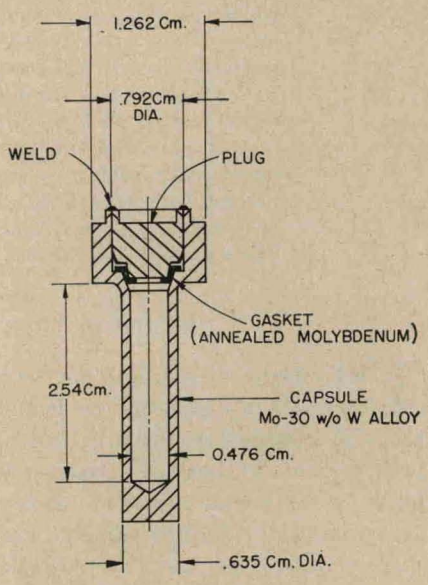

FIG. 1. Capsule for containment of alkali metals.

[2] F. Birch, Phys. Rev. 41, 641 (1932).

[3] J. M. Hochman and C. F. Bonilla, "The Saturated Vapor and Liquid Density of Cesium to 3000°F and the Critical Point of Cesium," USAEC Rept. No. CU-2660 (1965).

[4] A. V. Grosse, Research Institute of Temple University (private communication, 1963).

[5] M. G. Manzone and J. C. Briggs, "Less Common Alloys of Molybdenum," Climax Molybdenum Company (1962).

[6] R. Carlander, "The High Temperature Corrosion Resistance of Hastelloy "B" and Molybdenum to Rubidium," USAEC Rept. No. ORNL-CF-56-8-85 (14 August 1956).

[7] W. D. Weatherford, Jr., J. C. Tyler, and P. M. Ku, "Properties of Inorganic Energy-Conversion and Heat-Transfer Fluids for Space Applications," WADC-TR-61-96 (November 1961).

[8] M. J. Slivka, "A Study of Cesium Vapor Attack on Thermionic Convertor Construction Materials," Advanced Energy Conversion 3, 157 (1963).

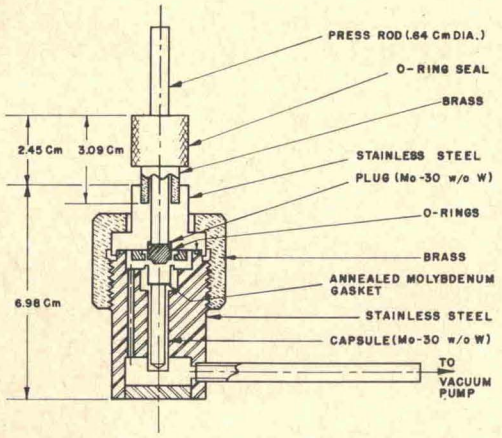

FIG. 2. Capsule charging assembly.

The capsule was charged with a weighed amount of material from the ampoule, evacuated, and then sealed under vacuum by deforming the molybdenum gasket by driving the tapered plug down with the pressing rod (Fig. 2). The sealed capsule was then removed from the capsule charging assembly and welded as shown in Fig. 1.

The capsule was contained in a cylindrical block of molybdenum-30 wt.% tungsten. The original design of the block called for a 3.08 cm diam×15.2 cm long cylinder in three pieces. The three pieces were held in fixed position inside a tantalum can by guide pins. The center piece was drilled radially to hold the capsule. The capsule was held in place by threaded end plugs. Since these plugs tended to seize under the extreme pressures and temperatures of the experiments, an improved design involving a two part split work piece was constructed (Fig. 3). This included a tapered Mo-30 wt.% W block of slightly over 3.08 cm diameter held in place by a 7.62 cm diam sleeve. This afforded more strength and easier removal of the capsule after heating. The work piece was contained in a 0.076 cm thick tantalum can to prevent reaction of the insulation with the molybdenum-tungsten block. The assembly was insulated by 6 μ diam tungsten carbide powder inside a silicon carbide crucible. Silicon carbide crucibles were chosen after testing alumina, magnesia, and zirconia crucibles which tended to crack and disintegrate with little use. Ceramically bonded alpha silicon carbide has a high thermal conductivity plus a low coefficient of thermal expansion and high strength all of which contribute to excellent thermal shock resistance.[9] These silicon carbide crucibles have shown no apparent change in strength or appearance after many (20–50) thermal cycles of the workpiece from room temperature to 2000°K (crucible temperature reached 1500°K maximum). A crucible lid made of Fiberfrax (an alumina-silica insulation made by the Carborundum Co.) held the powder in place. The crucible was supported by a fired lava (hydrous magnesium silicate made by American Lava Corporation) stand which was adjustable in the vertical dimension. As shown in Fig. 3, beam holes and thermocouple holes extending through the work pieces were connected to 0.64 cm tantalum tubing which extended out through the top and bottom of the crucible. The two 0.64 cm diam tantalum tubes extending from the beam holes lined up with two Veeco vacuum fittings in the wall of the vacuum tank. The Veeco fittings contained 1.27 cm stainless steel tubing sealed with a 0.025 cm stainless steel cap which permitted the radiation to pass with little attenuation.

The counting equipment outside the vacuum tank consisted of a single channel analyzer and associated equipment. This equipment included two high voltage sources, two preamplifiers, a scaler, two 2.54×2.54 cm NaI thallium activated crystals packaged with photomultiplier tubes and a recorder.

Selection of Gasket Material for Sealing Capsules

The three criteria for selection of a gasket material for forming the original capsule seal quickly limited the available materials. These three criteria were as follows:

(1) Vickers hardness number less than 350;
(2) resistant to alkali metal corrosion at 2000°C; and
(3) no high energy (>0.5 MeV) gamma produced by neutron irradiation.

Application of these three criteria limited the choice of materials to two; namely, annealed molybdenum and annealed rhenium. Tests of annealed rhenium showed that it was too hard and did not deform properly. Consequently, annealed molybdenum was chosen as the gasket material

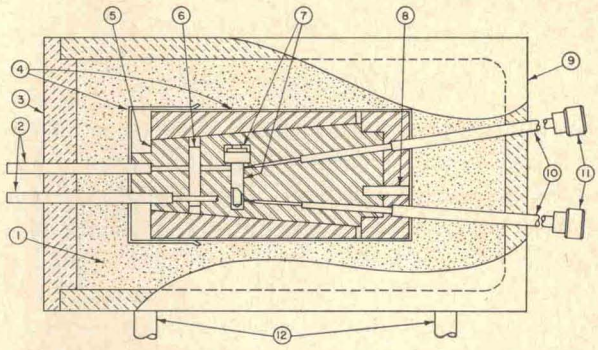

FIG. 3. Induction furnace assembly for vapor-liquid density measurements; 1—insulation; 2—tantalum tubes (0.64 cm o.d.) connecting to temperature measurement holes; 3—Fiberfrax lid; 4—tantalum can and lid; 5—tapered Mo-30 wt.% W cylinder in 7.62 cm o.d. Mo-30 wt.% W sleeve; 6—locating pin; 7—capsule containing test materials (see Fig. 1); 8—location pin; 9—silicon carbide crucible (16.5 cm o.d.×27.9 cm high×1.27 cm wall); 10—tantalum tubes (0.64 cm o.d.) connecting to collimation holes; 11—fitting mounted in vacuum tank wall and sealed with 0.025 cm diaphragm; and 12—refractory supports.

[9] F. C. Roe and E. D. Kwasniewski, Chem. Eng. Progr. **60**, No. 12, 97 (1964).

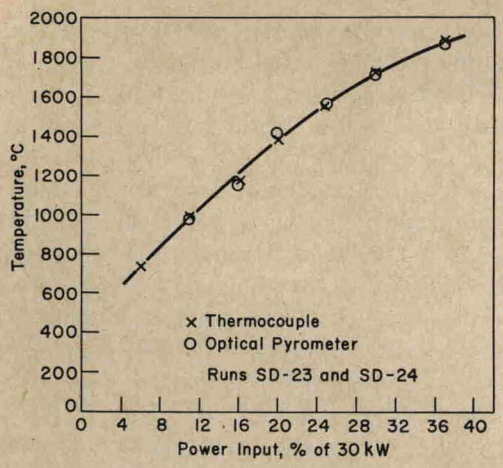

FIG. 4. Comparison of tungsten-5% rhenium/tungsten-26% rhenium thermocouple readings with optical pyrometer readings.

and it performed quite well for alkali metals. For measurement of densities of other metals, different criteria might apply so that other materials could be used for a gasket.

Temperature Measurement

Temperatures were measured by tungsten-5% rhenium/tungsten-26% rhenium thermocouples. These were calibrated using a model 8622-C Leeds & Northrup optical pyrometer. This pyrometer was calibrated with a standard tungsten lamp filament and against a standardized pyrometer. Maximum error in comparison with the other pyrometer and the tungsten lamp was less than 10°C. The pyrometer was then used to check the calibration of thermocouples over the temperature range 700 to 1900°C. A typical calibration curve is shown in Fig. 4. A standard procedure in obtaining the data was to calibrate thermocouples before and after a run to be certain there was no "drift" in thermocouple voltage with repeated temperature cycling.

Radiation Counting Technique

The radioactive tracer technique is based on the fact that small amounts of material may be measured accurately by radioactive counting techniques. Where the tracer isotope is homogeneously distributed through the phase being measured (as in this case) the radioactive count rate is directly proportional to the amount of material present if self-absorption is negligible. Measurements of radioactive count rate of the liquid were compared with density determinations by known standard techniques at lower temperatures (25 to 1300°C) and the relationship between radioactive count rate and density was shown to be constant. This was checked also with the capsule in an inverted position and the same relationship prevailed. This showed that the geometries of the vapor and liquid beam paths were the same. It may readily be shown[10] that the effect of self-absorption is as follows,

$$A_c = R(a\mu r\rho^3 + b\mu^2 r^2\rho^2 + \rho) = R\rho f, \quad (1)$$

where A_c is the activity measured at counter, R the geometry factor determined experimentally by counting liquids of known density, μ the gamma ray absorption coefficient (cm^2/g), r the radius of cylinder (cm), a, b the proportionality constants, ρ the density of material (g/cc), and f the self-shielding factor or fraction of activity escaping. The fraction of activity escaping can be seen to be

$$f = a\mu r\rho^2 + b\mu^2 r^2\rho + 1. \quad (2)$$

For the alkali metals, values of μ are much less than 1 and at high temperatures the density ρ is less than 1. Therefore, for the alkali metals at high temperatures, f is equal to 1 and self-shielding is negligible.

The counting equipment described above was calibrated using irradiated standards. Standards chosen for calibration of the equipment for counting some alkali metals were the following:

Element	Form of standard
Cesium	Cesium nitrate salt
Rubidium	Rubidium metal
Potassium	Potassium nitrate salt
Sodium	Sodium nitrate salt

These standards were irradiated in the CP-5 research reactor at Argonne National Laboratory so as to give a counting of about 50 000 counts/min. The counting rates and spectra determined on a single channel analyzer agreed well with those reported by Crouthamel.[11]

Errors in the counting technique included the usual factors of geometry and statistics and the additional factor of alignment of the beam holes. The source was made sufficiently active so that the counting rate was always greater than 5000 counts/min. Conversion to density from counts per minute was made on a comparative basis; thus, many factors such as geometry and resolving time were eliminated. Variations in efficiency were guarded against by counting standards at frequent intervals during the runs to see that the absolute counting rates did not vary.

OPERATION

Operating Steps

The twelve basic steps in making a run are as follows:

(1) Charging material to the capsule.
(2) Testing the capsule for integrity by heating to 1275°C.

[10] I. G. Dillon, Ph.D. Thesis, Illinois Institute of Technology (1965).
[11] C. E. Crouthamel, *Applied Gamma-Ray Spectrometry* (Pergamon Press, Inc., New York, 1960).

(3) Irradiating the charged capsule in CP-5 reactor.
(4) Cooling the capsule the necessary length of time.
(5) Charging the capsule to the work piece.
(6) Charging the workpiece to the furnace assembly.
(7) Evacuating the vacuum tank.
(8) Heating the furnace assembly to a predetermined steady state temperature.
(9) Recording temperatures; recording vapor and liquid activity by counting on a single channel analyzer.
(10) Adjusting induction heating controls to obtain a new higher steady state temperature and then repeating step (9).
(11) Cooling the furnace to room temperature.
(12) Removing the furnace assembly from the vacuum tank for disassembly and recharging.

In runs which were made to determine the density of alkali metals, charging the capsule involved the use of a high purity inert atmosphere (helium containing <10 ppm total H_2O+O_2) glovebox and the capsule charging assembly shown in Fig. 2. The desired amount of alkali metal was charged to the capsule body using a 1 cc hypodermic syringe for cesium (which melts at 28°C) and using a scalpel for rubidium, sodium, and potassium (solids at room temperature). The amount of material charged was determined by weighing on an Ainsworth analytical balance contained within the glovebox. After the alkali metal was charged to the capsule body, the capsule body, gasket, and plug (Fig. 1) were placed in the capsule charging assembly and the capsule was sealed under a vacuum of 20 μ. Final closure was made by Heliarc welding of the capsule as shown in Fig. 1.

The capsule was tested for integrity by heating to 1275°C in the inductively heated furnace assembly contained in the vacuum tank. The capsule was reweighed after heating to ascertain if any alkali metal had escaped. If the capsule were found to be sound, it was submitted to the CP-5 research reactor for irradiation to a calculated level of activity. The radioactive isotopes used in determining the critical constants of alkali metals are shown in Table I. This reactor can perform irradiations at thermal neutron fluxes up to 5×10^{13} n/cm^2 sec. In order to obtain a reading of about 100 000 counts/min at the counter, it was necessary to irradiate the alkali metal to a level of about 50 mCi of activity (2×10^9 disintegrations/sec).

After the irradiated capsule was removed from the reactor in cases where cesium and rubidium were irradiated, the capsule was cooled for about 20 days to permit decay of the 1 day ^{187}W and the 2.75 day ^{99}Mo produced by irradiation of the Mo-30 wt.% W capsule containing the alkali metal. Longer cooling times would be allowable for cesium (2.1 year half-life) and some other materials with long half-lives. Much shorter times were required for sodium (15 h half-life) and potassium (12.5 h half-life).

TABLE I. Radioactive isotopes used in determining critical constants of alkali metals.

Isotope	Half life	Gamma energy Mev	Precursor (n,γ) reaction	Abundance of precursor %	Thermal neutron cross section b
^{86}Rb	18.7 days	1.08	^{85}Rb	72.5	1
^{134}Cs	2.1 years	0.605	^{133}Cs	100	28
^{42}K	12.5 h	1.53	^{41}K	6.88	1.1
^{24}Na	15.0 h	2.75	^{23}Na	100	0.53

Sodium and potassium can be run after 1 day cooling of the capsule because their high energy gamma activities (>1.5 MeV) can be counted without interference from ^{187}W(0.7 MeV) and ^{99}Mo(0.74 MeV). When the capsule was sufficiently cooled, it was charged to the work piece. When the capsule was placed inside this work piece the radioactivity measured at the surface of the work piece was reduced by a factor of 10 from the activity measured at the surface of the capsule. When the capsule was placed inside the split design work piece (Fig. 3), the radioactivity was reduced by a factor of 15. The work piece was then charged to the furnace assembly which consists of the silicon carbide crucible and tungsten carbide insulation held in place by a Fiberfrax lid on the crucible. The crucible was supported by a lava stand adjustable in the vertical dimension. The assembly was heated by a 5 turn water cooled copper induction coil made of flattened 1.27 cm diam cooper tubing. Power was supplied by either a 30 kW or a 15 kW high frequency (10 kc) motor generator.

Prior to heating, the vacuum tank was evacuated to a pressure of less than 1 μ using the Stokes Microvac roughing pump and diffusion pump. When a suitable vacuum was obtained, the motor generator was started and the high frequency power turned on at such a value of power input that the rate of degassing of the insulation would not cause excessive pressure rise. The furnace assembly was heated to the desired temperature and when a constant tempera-

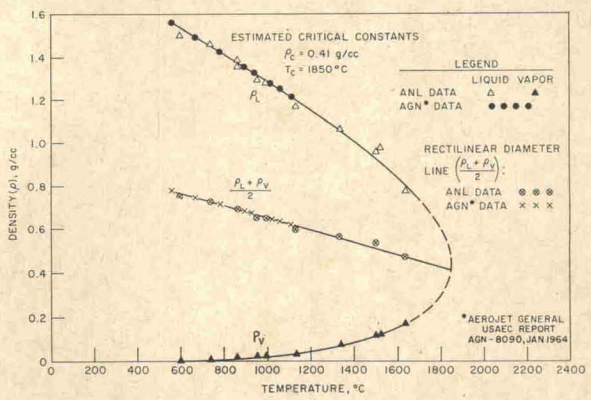

FIG. 5. Rectilinear diameter plot of vapor and liquid densities for cesium.

ture was attained, readings were taken every 5 min of (1) activity emanating from the vapor phase, (2) activity emanating from the liquid phase, and (3) temperature as measured by the tungsten-5% rhenium/tungsten-26% rhenium thermocouples. At least four separate 5 min counts were taken of the activity from each phase.

When sufficient data had been taken at any one temperature, the power input was increased and the data taking procedure was repeated at the new higher temperature. As soon as the run was completed, the power was turned off and the unit cooled to room temperature. The furnace assembly was then removed from the vacuum tank, disassembled and a new charge was made. Typical density data obtained by this method are shown in Table II and

TABLE II. Density data for cesium obtained by a radioactive counting technique.

Temperature °C	Vapor density g/cc	Liquid density g/cc: This work	Liquid density g/cc: Data of Hochman and Bonilla[a] (Electrical conductivity method)	Liquid density g/cc: Smoothed data of Hochman and Bonilla[a]
1220	0.043	1.142	1.208	1.136
1325	0.065	1.080	1.084	1.063
1437	0.090	0.990	1.022	0.980
1551	0.120	0.895	0.962	0.899
1640	0.170	0.785	0.830	0.829

[a] See Ref. 3.

Fig. 5. Figure 5 is a rectilinear diameter plot of the type developed by Cailletet and Mathias.[12] The density data of Aerojet General (AGN) shown in Fig. 5 were obtained by a dilatometer technique.[13] Comparison of AGN data with the lower temperature data of this study shows good agreement and indicates the high degree of accuracy of the radioactive counting technique.

DISCUSSION

The radiation counting method outlined in this paper has been demonstrated by obtaining vapor and liquid densities of alkali metals from room temperature up to near the critical point using the high temperature-high pressure cells previously described. The cells performed well their function of high temperature containment and shielding. This radiation counting method of obtaining densities is general in nature and applicable to determination of vapor and liquid densities for many substances. Data obtained by this method agree well with the only available high temperature (>1250°C) measurements of other investigators, namely Hochman and Bonilla's electrical conductivity measurements on cesium.[3] Hochman and Bonilla estimate their accuracy as ±5%. If the substance were not activated by neutron irradiation, an attenuation method might be used. This would involve directing a collimated beam of radiation from a radioactive source through the material.

ACKNOWLEDGMENTS

The Chemical Engineering Division of the Argonne National Laboratory, under the direction of R. C. Vogel, and the Chemical Engineering Department of the Illinois Institute of Technology, under the chairmanship of Prof. R. E. Peck gave much encouragement in this investigation. In particular, L. Burris and R. D. Pierce of the Chemical Engineering Division gave this investigation their enthusiastic support. The authors are grateful to members of the Drafting Group, A. Kelecius and R. Duda, who prepared shop drawings of the furnace assembly, and H. Smith who gave several useful design suggestions during the course of the work. Many of the components were built by the Central Shops of the Argonne National Laboratory. R. Flegel and B. Stanis of Central Shops contributed much in fabrication and suggestions of design modifications.

[12] L. Cailletet and L. Mathias, Compt. Rend. **102**, 1202 (1886).
[13] P. Y. Achener, "The Determination of the Latent Heat of Vaporization, Vapor Pressure, Enthalpy, Specific Heat, and Density of Liquid Rubidium and Cesium up to 1800°F," USAEC Rept. No. AGN-8090 (January 1964).