Saturation Pressures of Cesium to Temperatures and Pressures Approaching Critical State

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Saturation pressures were experimentally extended for cesium with use of a static method and a tantalum-alloy apparatus with a metal diaphragm as a pressure-sensing device. Vapor pressure equations of the Kirchhoff-type accurately represent the observed data for an extended temperature range from the normal boiling point to 3026° F, and the log *T* term is shown statistically to be required.

The alkali metals, because of their high latent heats of vaporization and their high heat-transfer coefficients, are attractive as high-temperature working fluids and coolants for turbine converters, thermionic power generators, MHD power systems, heat pipes, and various heat transport systems. Maximum temperatures are limited presently by material problems; however, with future improvements, applications for the alkali metals at higher temperatures should increase in order to take advantage of the higher thermodynamic efficiencies.

To evaluate the high-temperature performance of the metals, a reliable body of experimentally determined properties will soon be required to temperatures and pressures approaching the critical state of each metal. In 1966, Stone *et al.* (*9*) published saturation pressures for sodium, potassium, and cesium to temperatures of 2540°, 2400°, and 2350° F, respectively. Additional measurements made recently for cesium overlap the temperature range of the previous measurements and extend the data to a temperature within about 200° F of the critical value.

METHODS

The saturation pressures reported here were measured as a part of superheat studies. Measurements in both the saturation and superheat regions were made with small closed chambers with flexible metal diaphragms as pressure sensors.

Procedure. At each equilibrium temperature, the pressure of argon external to the measurement chamber was adjusted so that the diaphragm was just making or breaking electrical contact with an insulated probe. Under these conditions, the pressure of inert gas (except for a small deflection correction which was always below 0.1 psi) was equal to the pressure of the cesium vapor, and was observed externally at room temperature with Bourdon-tube gages. To provide high accuracy for the full-pressure range, five 12-inch precision gages were used with ranges of 50, 150, 500, 1500, and 2500 psi. They were calibrated *in situ* with dead-weight piston gages by personnel of the Eastern Standards Laboratory. Experimental pressures were recorded from the most sensitive gage in range.

The method is similar to that previously described (*9*, *10*). However, major changes in materials and techniques were necessary to meet the conditions imposed by higher temperatures and pressures. The new measurement chamber and diaphragm (Figure 1) were fabricated from a tantalum alloy (10% tungsten, 2% hafnium), and high-purity beryllia were used to electrically insulate the probe. The sensitivity of the 5-ml-thick diaphragm was shown experimentally to remain unchanged after cycling from room temperature to 3400° F. The machining and welding characteristics of the tantalum alloy were equal to those of the columbium alloy used for the previous measurements (*10*).

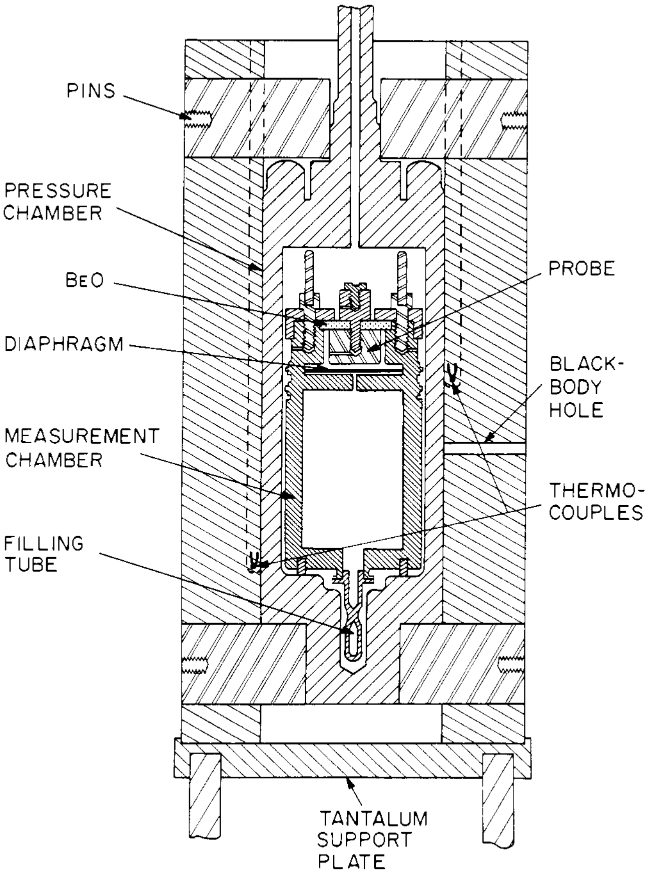

Figure 1. Vapor pressure measurement apparatus

The measurement chamber was positioned inside a larger chamber of tantalum-10% tungsten, which, in turn, was backed with a heavy-walled tungsten tube to control radial creep. One-inch diameter tantalum alloy pins were inserted at both ends to control axial creep. These precautions were taken since the tantalum alloys have only moderate creep strengths above 3000° F.

The entire measurement system with its tungsten resistance furnace was enclosed in an 18-inch stainless steel chamber and operated under vacuum. The legs supporting the measurement system were positioned on a plate and screw jack (not shown in Figure 1) to permit the entire apparatus at temperature to be moved up or down, relative to the heating element, to obtain isothermal conditions for each experiment.

Two thermocouples with elements of tungsten-3% rhenium and tungsten-25% rhenium were positioned (Figure 1) with their junctions opposite the two extremes of the measurement chamber. They were insulated with beryllia, sheathed in small diameter tantalum tubing, and protected with an atmosphere of argon. All measurement thermocouples were cut from 50-foot rolls of the two tungsten-rhenium alloys and indirectly calibrated at the National Bureau of Standards by the direct calibration (1450° to 3450° F) of couples from the ends of the rolls. Calibration differences for the two couples ranged from 0.00 mv at 1450° F to 0.02 mv at 3450° F.

All temperatures reported here were measured with thermocouples. However, to increase the reliability of the measurement, equilibrium temperature readings were also made with an automatic optical pyrometer sighted on a black-body hole. This pyrometer and the glass window in the optical path were calibrated at NBS. The average difference in temperature as obtained by the two methods was only 0.14%, and the selection of temperatures obtained by one method over the other was arbitrary.

The cesium used in all tests was of high-purity grade from MSA Research Corp. Metal samples were distilled under high vacuum from a glass retort into tantalum alloy ampoules for subsequent transfer to the measurement chamber in an inert gas handling box. A typical spectrographic analysis of the alkali metal after one distillation is presented in a previous article (*9*). Volatile and nonvolatile impurities are present in concentrations too low to produce a measurable vapor pressure change.

RESULTS

Three superheat experiments were performed. For each, equilibrium measurements of pressure and temperature were obtained along the saturation curve, and observed vapor pressures are recorded in Table I. An equilibrium condition for each determination was assured by taking multiple readings of temperature and pressure at 5- to 10-minute intervals until successive readings showed a temperature drift less than 0.2° F per minute. The temperature gradient along the axis of the measurement chamber was controlled within 1° or 2° F per cm.

Table I. Saturation Pressures of Cesium

Temp., ° F	Pressure, Abs Atm	Temp., ° F	Pressure Abs Atm
1551.9	4.153	2489.4	42.794
1734.6	7.625	2642.4	54.651
1738.8	7.695	2837.5	72.346
1922.7	13.143	3026.5	92.216
2084.9	19.703	1578.9	4.434
2272.5	29.627	1923.8	12.908
2475.1	42.758	2322.3	31.879
2705.0	61.595	2631.7	53.811
1627.0	5.157	2653.5	56.097
1729.4	7.317	2465.4	41.603
1931.4	13.087	2136.7	22.040
2111.7	20.458	1582.9	4.621
2316.0	31.308	...	...

It has previously been shown (*6, 10, 12*) that saturation pressures observed in closed containers at temperatures near the intersection of the saturation and superheat curves are invariably below corresponding results on the true saturation and superheat curves. This phenomenon is observed for short temperature ranges of 50° F or less. For the three NRL experiments reported in Table I, two points were in the depressed regions and are not included in the table.

Since the results for cesium reported here overlap and extend our previous measurements, both sets of data were treated as a composite. It was found that all results could be effectively fitted for the full temperature range with the equation

$$\log p = 5.87055 - 7036.2/T - 0.5329 \log T \qquad (1)$$

where p is pressure in absolute atmospheres, and T is temperature in ° R. The value of 0.5329 for the coefficient of the log T term was selected from the lower temperature analysis (*9*) and obtained with values of pressure equally weighted over the temperature range. The value of this coefficient was not significantly changed by the addition of the higher temperature results.

To evaluate the precision of the vapor-pressure measurements and to establish statistically the necessity for the log T term, one least-squares equation was generated with the log T term, and another without it. The derived coefficients for both equations are presented at the top of Table II along with their corresponding precision indices. The deviation figures reveal that the log T term has definite statistical significance and that the Kirchhoff form should be used.

$$\log p = 5.87303 - 7040.7/T - 0.5329 \log T \qquad (2)$$

Equation 2 is the vapor-pressure equation derived previously (*9*) from the lower temperature information. Deviations of the composite data from Equation 2 are presented on the bottom line of Table II for direct comparison with the deviations from Equation 1. Obviously, the two equations are effectively identical and the results in this article are consistent with the earlier ones. Equation 1 is preferred since it alone was generated from data covering a temperature range of 1236° to 3026° F.

DISCUSSION

Two other experimental determinations of the vapor pressure of cesium to the critical temperature, or to temperatures approaching this point, have been reported by Hensel and Franck (*5*) and Silver (*8*). For overlapping temperature ranges above 2600° F, there is reasonably good agreement among the three sets of data; differences in corresponding pressures are generally less than 2%. At lower temperatures, the vapor pressures of Silver (*8*) are lower than those of NRL, differing by about 4.8% at 2400° F.

There are several other existing vapor-pressure measurements at lower temperatures, and these results at temperatures above the normal boiling point may be compared with those in this article. The vapor pressures reported by Shpielrain (*7*), Tepper (*11*), Achener (*1*), Bonilla (*3*), and Bohdansky (*2*) show average deviations from Equation 1 of 0.4, 1.4, 1.5, 3.8, and 4.1%, respectively.

Ewing *et al.* (*4*) generated consistent vapor-pressure equations for several alkali metals, including cesium, for a temperature range of 400° to 2400° F by treating each metal vapor as a mixture of monomeric and higher molecular weight species. The same technique of analysis and correlation could not be applied to these higher temperature cesium

Table II. Derived Coefficients for Vapor Pressure Equation of Cesium

$\log p = A + B/T + C \log T$

Data Used in Deriving Coefficients[a]	Coefficients			Deviations of Composite Data	
	A	B	C	Std Dev, $\log p$	Std %, Dev/p
X	5.87055	−7036.2	−0.5329	0.0035	0.80
X	3.84993	−6516.8	0	0.0046	1.06
Y	5.87303	−7040.7	−0.5329	(0.0035)	(0.81)

[a] X, Composite of low temperature data (*9*) and high temperature data (this publication); Y, low temperature data (*9*).

results since no equation of state has been obtained for this range.

A review of a previous paper, where a closed-chamber diaphragm method (*10*) was also used, suggested that the depression phenomenon observed at the intersection of the saturation and superheat curves might be explained by a combination of effects—an undetected temperature gradient along the axis at the lower extremity of the measurement chamber (at the filling tube) and the diminishing amount of liquid phase. This possibility was checked experimentally in the low temperature system (*10*) by making saturation measurements in this region with a thick metal cap installed over the filling tube and by inducing large temperature gradients along the axis of the chamber. The results of these tests showed conclusively that the vapor pressure lowering was not associated with thermal gradients on the apparatus. It is believed that the pressures are lowered by some physical phenomenon in combination with the diminishing liquid phase and that they do not represent true saturation values.

A discussion of the diaphragm method using columbium alloy for measuring vapor pressures at temperatures to 2400° F was presented by Stone *et al.* (*10*). The present study has shown that this method may be successfully extended to at least 3400° F with use of tantalum alloys. The 5-ml-thick diaphragms used in this study had free diameters of 1.25 inches and were found to perform reproducibly with high sensitivity for at least two full temperature cycles. Since one possible source of error was the diffusion of argon through the thin diaphragms at higher temperatures, it was demonstrated experimentally (by checking the chamber for gas content at the conclusion of each experiment and by the reproducibility of observed pressures at lower temperatures) that no significant diffusion had taken place.

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Vapor Pressure of D_2O from 106 to 300° C

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Although there have been many measurements of the vapor pressure of heavy water, the data in a substantial middle range of temperatures appear to be of lower precision and more questionable accuracy than the data at higher or lower temperatures. Figure 1 shows ranges covered by several of the better known investigations (*1, 2, 4, 9–15*). Although Miles and Menzies (*9*) and Riesenfeld and Chang (*13*) obtained results below 100° C in reasonable accord with a recent, careful study (*2*), their work at higher temperatures has several disturbing features. For example, in extending their measurements to pressures over 1 atm, Miles and Menzies used a cruder apparatus and techniques subject to greater error. Also, the Riesenfeld and Chang data scatter a good deal more at the higher temperatures than below 150° C. Finally and most importantly, both these early studies seem to have been subject to some systematic error at higher temperatures, for they both gave estimates of the crossover temperature (at which the vapor