tive merits of this method is of interest. Since the boiling point apparatus, in various modifications, is so often used with liquids for the measurement of saturation pressures, it is appropriate to compare it with the null-point technique.

The several sources which generally contribute to error in measuring vapor pressures are: temperature measurement, pressure measurement, volatile and nonvolatile impurities, method of selection of the equilibrium temperature for the observed pressure, superheating of the liquid, and Poynting effect. The first three sources are common to all vapor-pressure methods and errors may be controlled by the choice and calibration of measuring devices and by control of the purity of the material being measured. In many measuring devices, particularly of the boiling point type, a temperature difference exists along the length of the apparatus, and errors can be generated by superheating of the liquid, by undetected cold spots, or by a subjective selection of the equilibrium temperature. If the null-point apparatus is designed of short length and large bulk, the complete apparatus may be maintained at the same temperature during a pressure measurement, and no choice as to equilibrium temperature is required. In most apparatus of the boiling point type, an inert gas is used in contact with the vapor and unless proper precautions are taken, error can be generated by diffusion of the inert gas to the surface of the liquid. Since no filling gas is in contact with the contact with the vapor in the null-point apparatus, there can be no Poynting effect.

There are, as one might expect, sources of error which are peculiar to the null-point apparatus. These include: the diffusion of gases through the diaphragm at higher temperatures, the inclusion of inert gas in the chamber during the welding off operation, and sensitivity corrections to the diaphragms. These have been rather fully discussed (*10*), and it has been demonstrated that with the Cb–1%Zr apparatus, these sources of error can be controlled at very low levels.

ACKNOWLEDGMENT

The authors are grateful to the National Aeronautics and Space Administration for support of this work. They also thank Janet P. Mason or the NRL Applied Mathematics Staff for computer programming and Samuel H. Cress of the NRL Metallurgy Division for spectrochemical analyses of metal samples.

LITERATURE CITED

(1) Achener, P.Y., "Determination of the Latent Heat of Vaporization, Vapor Pressure, Enthalpy, Spceific Heat, and Density of Liquid Rubidium and Cesium up to 1800° F.," Aeroject-General Nuclenoics, **AGN-8090** (January 1964).

(2) Bonilla, C.F., Sawhney, D.L., Makansi, M. M., *Trans. ASME* **55**, 877 (1962).

(3) Bowles, K.J., Rosenblum, L., Natl. Aeronaut. Space Admin., **NASA TN D-2849** (May 1965).

(4) Grachev, N.S., Kirilov, P.L., *Inzh. Fiz. Zhur.* **3**, 62 (1960); (trans.) **NASA II F-66.**

(5) Grey, Peter, "Second Symposium on Thermophysical Properties," A.S.M.E., Princeton, N. J., January 1962.

(6) Kirilov, P.L., Grachev, N.S., *Inzh. Fiz. Zhur.* **2**, 3 (1959); NRL Trans. **805.**

(7) Makansi, M.M., Madsen, M., Selke, W.A., Bonilla, C.F., *J. Phys. Chem.* **60**, 128 (1956).

(8) Makansi, M.M., Muendel, C.H., Selke, W.A., *Ibid.*, **59**, 40 (1955).

(9) Sowa, E.S., *Nucleonics* **21**, 76 (1963).

(10) Stone, J.P., Ewing, C.T., Spann, J.R., Steinkuller, E.W., Williams, D.D., Miller, R.R., J. CHEM. ENG. DATA **5**, 309 (1966).

(11) Tepper, F., Murchison, A., Zelenak, J., Roehlich, F., Thermophysical Properties of Rubidium and Cessium," MSA Research Corp., Rept. **ML-TDR-64-42** (May 1964).

(12) Thorn, R.J., Winslow, G.H., *J. Phys. Chem.* **65**, 1297 (1961).

(13) Walling, J.F., Nuzum, H.K., Lemmon, A.W., Jr., "Vapor Pressure and Heat of Vaporization of Potassium for 480° to 1150° C.," Battelle Memorial Institute, **BATT-4673-T3** (April 1963).

RECEIVED for review August 20, 1965. Accepted March 17, 1966.

High Temperature Specific Volumes of Liquid Sodium, Potassium, and Cesium

J. P. STONE, C. T. EWING, J. R. SPANN, E. W. STEINKULLER, D. D. WILLIAMS, and R. R. MILLER
U. S. Naval Research Laboratory, Washington, D.C.

The specific volumes of liquid sodium, potassium, and cesium (at saturation) were measured with pycnometers over the temperature ranges from 1577° to 2491°, 1099° to 2287°, and 1577° to 2304° F., respectively. The results are correlated with those published for lower temperatures, and the specific volume of each metal is well defined by a single equation from its melting point to the maximum temperature of the current measurements.

THE alkali metals are attractive as thermodynamic working fluids in advanced power converters. In order to evaluate the performance of the metals in turbines, boilers, and condensers, an increased knowledge of their liquid and vapor properties at higher temperatures is required. One objective of the program at this laboratory was to derive from *PVT* observations various thermodynamic properties (including Mollier diagrams) for sodium, potassium, and cesium vapors. In the reduction of the *PVT* data, the specific volume of each liquid metal from its normal boiling point to 2500° F. was required. Since there were no published values in the upper part of this range, measurements were undertaken and the results are reported here. This article is the third of a current series on the alkali metals and follows previous ones on *PVT* properties (*9*) and vapor pressures (*10*).

EXPERIMENTAL

The specific volume of each metal was determined pointwise using columbium-1% zirconium apparatus (Figure 1) with pycnometers of 30-cc. nominal volume. In preparation for a determination, the lower chamber (the pycnometer) was filled with the desired alkali metal by distillation and then moved to a controlled atmosphere box where it was welded to the overflow chamber, and this, in turn, was welded to a long tube, which supported the apparatus at the center of the furnace (*9*) and permitted pressurization with inert gas.

For an experimental determination, the apparatus was heated to the desired temperature with the excess metal spilling over through the 3/32-inch diameter capillary into the overflow chamber, and the weight of metal remaining in the known pycnometer volume was determined, after cooling, by weight difference and by titration. To prevent transfer by boiling of metal from the pycnometer to the overflow chamber, an overpressure of argon was maintained at all temperatures (1 atm. in excess of the saturation value of the alkali metal). Temperatures were measured with thermocouples attached at the top and bottom of the pycnometer chamber; and, to ensure an isothermal condition for each experiment, furnace heaters were adjusted so that these temperatures were matched within 2° F.

Many of the methods and techniques employed in this investigation were similar to those described in previous publications (*9, 10*), where information not included here on the refractory container alloy, pressurized furnace systems, temperature measurement techniques, and metal purification procedures may be found. The same high purity alkali metals described for the *PVT* study (*9*) were used.

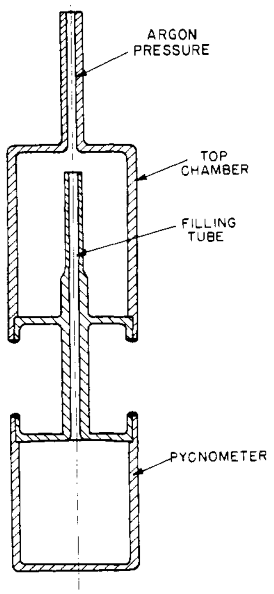

Figure 1. Specific volume apparatus

RESULTS AND DISCUSSION

The observed specific volumes of the three metals are presented in Table I. The experimental results effectively represent values at saturation conditions. Although the compressibilities of the liquid alkali metals are not known at these temperatures, an overpressure of only 1 atm. would not be expected to make a measurable change in volume. This was demonstrated experimentally by Tepper (*11*) when he showed that an overpressure of 7 atm. at 1650° F. had no effect on the liquid density of rubidium.

Table I. Specific Volumes of Liquid Sodium, Potassium, and Cesium

Temp., ° F.	Specific Volume, Cu. Ft./Lb.
Sodium	
1576.8	0.021396
1886.2	0.022766
2093.5	0.023683
2268.9	0.024606
2491.2	0.025685
Potassium	
1099.0	0.022751
1562.6	0.024999
1747.0	0.026084
1928.0	0.027267
2121.7	0.028644
2286.7	0.029801
Cesium	
1577.0	0.011826
1762.2	0.012467
1939.9	0.013112
2122.5	0.013919
2303.8	0.014883

The pycnometer method, although time-consuming, was chosen for these determinations because of its intrinsic accuracy. There were only three quantities to be measured—volume, weight, and temperature—and each could be obtained with high accuracy. A different pycnometer was used for each result, and its volume was obtained by precise dimensioning at room temperature. Corrections for thermal expansion were applied using experimentally determined linear expansion data (*9*), and the maximum error in the final volume at temperature did not exceed ±0.2%. It was recognized that any permanent deformation of the Cb-1% Zr chamber during a temperature cycle would introduce additional error. However, it was shown by redimensioning several chambers that any changes were within the dimensioning accuracy. This exceptional volume stability can probably be attributed to the procedure of balancing the internal and external pressures on each chamber. The weight of metal remaining in the known volume was determined by weight difference and by acidimetric titration for total alkalinity following reaction with alcohol. Although the difference between these two methods was never more than 0.1%, the reported values are those determined by weight difference, since they are believed to be the more accurate. Temperatures were measured with Pt 6% Rh-Pt 30% Rh thermocouples, which were calibrated by the methods described (*9*) and checked for stability by the technique described by Walker, Ewing, and Miller (*14*). Error in temperature relative to the thermodynamic scale should not exceed 0.14% at 2500° F. If one includes all known uncertainties, the probable error of the reported specific volumes range from ±0.25 to ±0.30%, depending upon the metal and the temperature.

Including previously published results, overlapping determinations for each metal have now been made from the melting point to the maximum temperature of the current measurements. An equation for each metal was derived by fitting the best curve to all published values, and the recommended equations are

$$1/v_{\mathrm{Na}} = 59.566 - 0.79504 \times 10^{-2}t - 0.2872 \times 10^{-6}t^2 + 0.06035 \times 10^{-9}t^3 \quad (1)$$

$$1/v_{\mathrm{K}} = 52.768 - 0.74975 \times 10^{-2}t - 0.5255 \times 10^{-6}t^2 + 0.0498 \times 10^{-9}t^3 \quad (2)$$

Table II. Summary of Specific Volume Measurements for Liquid Sodium, Potassium, and Cesium

Investigator and Reference	Method	Temp. Range, °F.	Av. Discrepancy of All Observed Values from Those Calculated with Eq. 1, 2, or 3, %
		Sodium	
NRL (*2*)	Dilatometric	M.p. to 503	±0.07
Jackson (*5*)	Buoyancy	937 to 1314	−0.74
Rinck (*8*)	Buoyancy	804 to 1183	±0.12
Hagen (*3*)	Dilatometric	M.p. to 336	±0.04
Novikov (*7*)[a]			
A	Buoyancy	248 to 505	−0.16
B	Buoyancy	275 to 1324	+0.67
Nishibayashi (*6*)	Buoyancy	486 to 1580	±1.06
NRL (this work)	Dilatometric (pycnometers)	1577 to 2491	±0.16
Tepper (*13*)	Dilatometric	411 to 2031	+0.68
		Potassium	
Hagen (*3*)	Dilatometric	M.p. to 230	+0.17
NRL (*2*)	Dilatometric	M.p. to 499	±0.05
Novikov (*7*)	Buoyancy	196 to 1352	±0.23
Jackson (*5*)	Buoyancy	257 to 1281	−0.77
Rinck (*8*)[b]	Buoyancy	617 to 1104	±0.48
NRL (this work)	Dilatometric (pycnometers)	1099 to 2287	±0.11
Tepper (*13*)	Dilatometric	477 to 2014	+0.80
		Cesium	
Achener (*1*)	Dilatometric (pycnometers)	83 to 1671	±0.73
Tepper (*12*)	Dilatometric	105 to 1950	±0.40
NRL (this work)	Dilatometric (pycnometers)	1577 to 2304	±0.14
Hochman (*4*)			
Low	Determination of volume in vertical tube by resistivity measurement	587 to 1529	±1.16
High		1926 to 2984	+6.79

[a] A. With steel sinker. B. With tungsten sinker. [b] Except for two results, data of Rinck show average discrepancy of ±0.21%.

$$1/v_{Cs} = 116.483 - 1.7520 \times 10^{-2}t - 1.6855 \times 10^{-6}t^2 \qquad (3)$$

where t is temperature in degrees Fahrenheit and v is specific volume in cubic feet per pound.

All the independent measurements for each metal are summarized and referenced in Table II. For each investigation, the temperature range, general method, and average discrepancy of observed values from those calculated with Equations 1, 2, and 3 are presented. In general, the several sets of measurements for each metal show good internal consistency, and it is believed the equations will give values accurate to ±0.6% between the melting point and the upper measured limits.

ACKNOWLEDGMENT

The authors are grateful to the National Aeronautics and Space Administration for support of this work.

LITERATURE CITED

(1) Achener, P.Y., Aerojet-General Nucleonics, Rept. **AGN-8090** (January 1964).

(2) Ewing, C.T., Atkinson, H.B., Jr., Rice, T.K., U. S. Naval Research Laboratory, Rept. **C-3287** (May 1948).

(3) Hagen, E.B., *Ann. Physik* **255**, 437 (1883).

(4) Hochman, J.M., Bonilla, C.F., "Saturated Liquid and Vapor Density of Cesium to 3000° F., and Critical Point of Cesium," Third Symposium on Thermophysical Properties, ASME, p. 122, March 1965.

(5) Jackson, C.B., Wieczorek, G.A., Van Andel, A., Mine Safety Appliances Co., U. S. Naval Research Laboratory Rept. **P-3010** (September 1946).

(6) Nishibayashi, M., WADC Tech. Rept. **53-308**, Part 1 (November 1953).

(7) Novikov, I.I., Solovyev, A.N., Khabakhpasheva, E.M., Gruzdev, V.A., Pridantsev,A.I., Vasenina, M.Y., *Atomnaya Energiya* 1, 92 (1956).

(8) Rinck, E., *Compt. Rend.* **189**, 39 (1929).

(9) Stone, J.P., Ewing, C.T., Spann, J.R., Steinkuller, E.W., Williams, D.D., Miller, R.R., J. CHEM. ENG. DATA **5**, 315 (1966).

(10) *Ibid.*, p. 320.

(11) Tepper, F., Murchison, A., Zelenak, J.S., Roehlich, F., MSA Research Corp. Rept. **ASD-TDR-63-133** (February 1963).

(12) *Ibid.*, **ML-TDR-64-42** (May 1964).

(13) Tepper, F., Zelenak, J., Roehlich, F., May, V., *Ibid.*, Rept. **AFML-TR-65-99** (May 1965).

(14) Walker, B.E., Ewing, C.T., Miller, R.R., *Rev. Sic. Instr.* **33**, 1029 (1962).

RECEIVED for review August 20, 1965. Accepted March 17, 1966.