

NRL Report 5964

UNCLASSIFIED

HIGH TEMPERATURE PROPERTIES OF SODIUM AND POTASSIUM

NINTH PROGRESS REPORT FOR PERIOD
1 OCTOBER TO 31 DECEMBER 1962

C. T. Ewing, J. P. Stone, J. R. Spann,
T. A. Kovacina, and R. R. Miller

Inorganic and Nuclear Chemistry Branch
Chemistry Division

May 20, 1963



U. S. NAVAL RESEARCH LABORATORY
Washington, D.C.

CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
SUMMARY OF EXPERIMENTAL PROGRAM	1
INDIVIDUAL PROPERTY TESTS	2
Pressure-Volume-Temperature	2
Saturated Vapor Pressure	7
Specific Heat	8
Equilibrium Solubilities of Columbium and Zirconium in Liquid Sodium	11
REFERENCES	13

ABSTRACT

An experimental program is in progress at this Laboratory to measure various thermophysical properties of sodium, potassium, and their vapors at elevated temperatures. Preliminary results presented in this report cover the following: pressure-volume-temperature data for vapor states of sodium between 960°C (1.9 atm) and 1420°C (25.1 atm); saturated vapor pressure of sodium from 1 to 25 atm; specific heat of saturated liquid sodium from 100° to 1170°C; and equilibrium solubilities of columbium and zirconium in liquid sodium from 802° to 1380°C.

PROBLEM STATUS

This is an interim report on this problem; work is continuing.

AUTHORIZATION

NRL Problem C05-15
NASA Contract Number NASA C-76320
(Solubility Study only partially supported by NASA C-76320)

Manuscript submitted April 26, 1963.

HIGH TEMPERATURE PROPERTIES OF SODIUM AND POTASSIUM

NINTH PROGRESS REPORT FOR PERIOD
1 OCTOBER TO 31 DECEMBER 1962

INTRODUCTION

In the development of compact, turboelectric systems, the National Aeronautics and Space Administration is sponsoring a property measurement program for the evaluation of several liquid metals as possible working fluids. As an integral part of this program, the U.S. Naval Research Laboratory is engaged in the measurement of several thermo-physical properties of sodium to 1370°C and potassium to 1150°C.

SUMMARY OF EXPERIMENTAL PROGRAM

The properties of sodium and potassium which are being determined experimentally include density, vapor pressure, specific heat, and pressure-volume-temperature (PVT) relationships. In addition, the surface tension of liquid potassium is to be measured from its melting point to 1150°C, and the equilibrium solubility of columbium and zirconium in liquid sodium (partially supported by C-76320) is being determined to 1370°C.

Heat capacity values for sodium have been obtained in the copper block calorimeter, and preliminary values are tabulated in this report. A topical report on this phase will be written upon completion of similar measurements on potassium.

Densities of liquid potassium and sodium at higher temperatures have been previously reported (1,2). Additional pycnometers have been prepared, and measurements at lower temperatures on both metals will be completed this fiscal year.

Problems associated with the null-point apparatus for the PVT measurements have been solved. Five successful experiments with sodium to temperatures as high as 1420°C have been made and the PVT curves presented in this report are plotted from uncorrected data. Although these experiments do cover the required superheat range from 960° to 1420°C, at least three additional experiments are required to complete this phase and only a cursory examination of the data has been made. Vapor pressures for sodium ranged from 1 atm at 882°C to 25.0 atm at 1416°C, and a preliminary curve is presented.

A radiochemical method was used to determine the equilibrium solubilities of the Cb-1%Zr alloy in liquid sodium to 1380°C. This work has been completed, and solubility results are reported.

The maximum bubble pressure apparatus which is to be used for surface tension determinations of liquid potassium (2) has been designed, and the machining work is being performed. These measurements will require modifications to one of the existing furnace systems and will be performed at the conclusion of the PVT tests.

INDIVIDUAL PROPERTY TESTS

Pressure-Volume-Temperature

PVT data for the vapor states of sodium between 960°C (1.9 atm) and 1420°C (25.1 atm) have been obtained. The Cb-1% Zr apparatus (Fig. 1) is a closed chamber of known volume equipped with a flexible (5 mil) diaphragm and charged with a known weight of

alkali metal. The position of the diaphragm is monitored with an electrical continuity circuit and controlled by balancing the internal and external pressures. A measurement of the vapor pressure of the alkali metal is then made externally with calibrated Bourdon-tube gages.

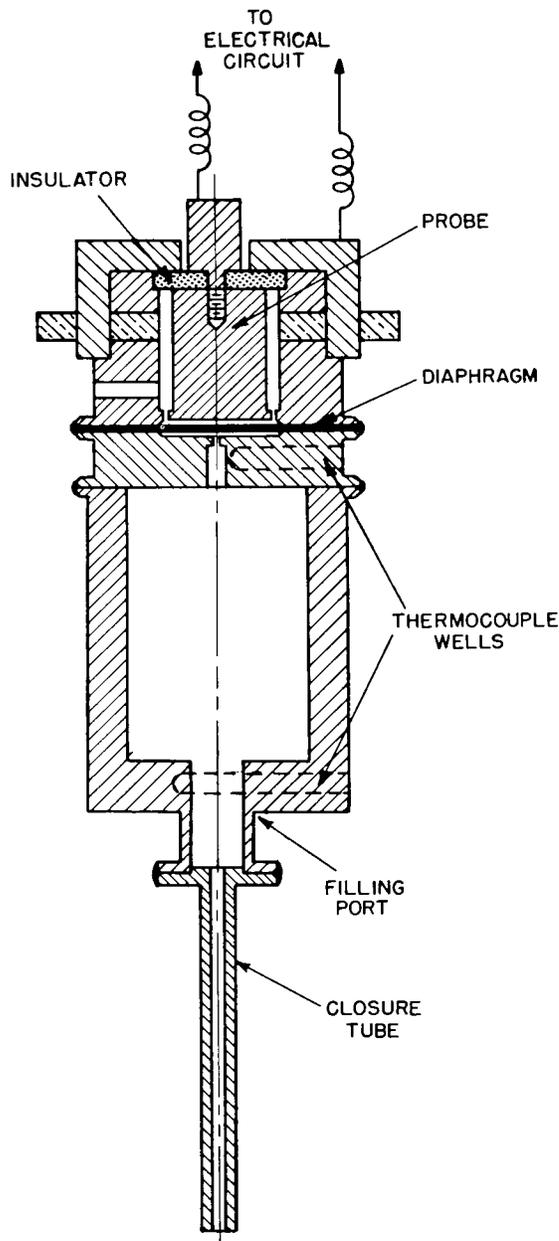


Fig. 1 - Null-point apparatus

Preliminary PVT data of five experiments are presented in Figs. 2 to 5. Each curve represents the saturated vapor pressure curve and the superheated vapor curve for a given weight of sodium added to a chamber with a nominal volume of 57 cc. The weight of sodium varied from a low of 28.14 mg for Experiment 4 to a high of 307.59 mg for Experiment 7. Although only a portion of the vapor pressure curve is shown for many of the experiments, equilibrium measurements of pressure and temperature for each experiment were made from the normal boiling point to at least 1370°C for no less than one complete heating and cooling cycle. Each such cycle required continuous operation of the equipment for a period of 52 to 60 hours.

For the highest pressure experiment (Fig. 5), a shift in the equilibrium pressure (at the same average temperature) could be obtained in the saturation region near superheat by introducing a temperature difference between the two ends of the chamber. The dashed curve represents equilibrium pressures obtained with the bottom of the chamber adjusted to a temperature several degrees higher than that of the top. It was evident from this data, that all remaining liquid was flashed to vapor as the maximum temperature at any point on the chamber approached superheat temperature. On the other hand, after the vapor reached superheat, pressure was a function of the average temperature of the chamber and was independent of temperature differences along

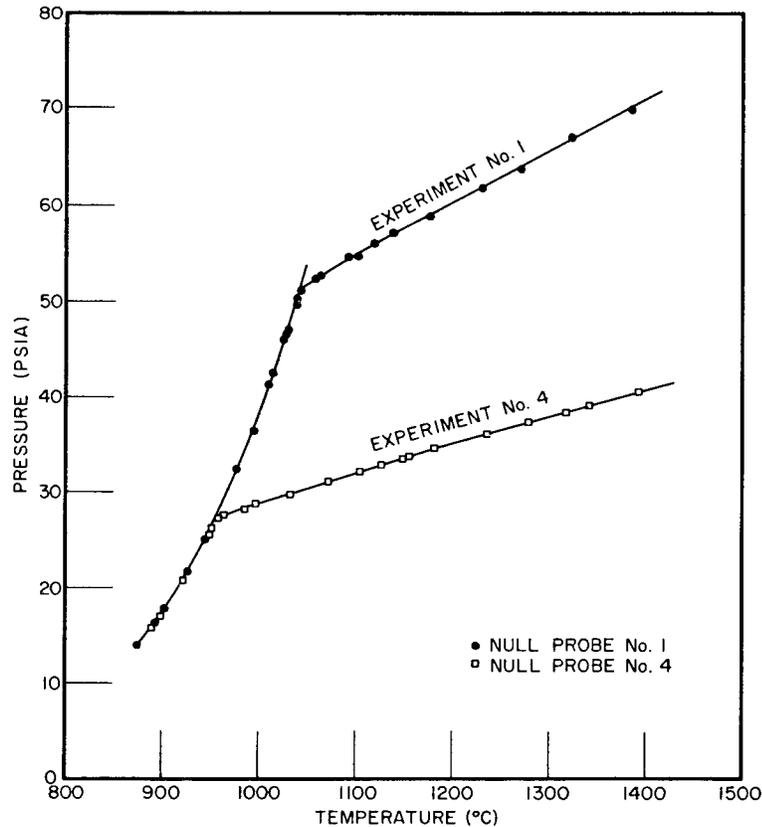


Fig. 2 - Pressure-volume-temperature data for sodium-null-point experiments

the chamber as high as 15°C. True saturation pressures are represented by the solid curve where the experimental points were determined under isothermal conditions.

The precision in the PVT measurements to permit accurate determinations of other thermodynamic quantities has been discussed in previous reports. The steps taken to insure high accuracy in the various measurement parameters are discussed in the following paragraphs. The actual magnitude of error to be expected in each parameter can be presented more reliably at the conclusion of all the measurements.

The position of the probe (Fig. 1) relative to the diaphragm is adjusted initially in each apparatus such that the final position of the probe is 2 to 4 mils above the diaphragm. The observed sensitivity of each diaphragm (with a free diameter of 1.5 inches) is between 0.05 and 0.10 psi per mil of deflection for a maximum deflection of 10 mils. Thus, the pressure inside the apparatus will be higher than that observed externally by approximately 0.1 to 0.2 psi. This excess pressure required for deflection of the diaphragm represents a small correction which must be applied to the observed pressure at each temperature. The magnitude of the correction for each diaphragm and apparatus is determined experimentally (at room temperature) at the conclusion of the alkali metal experiment.

Although the magnitude of the deflection correction is small (0.1 to 0.2 psi at room temperature), it is a function of sensitivity and is therefore temperature dependent. For the preliminary PVT results, observed pressures are adjusted at higher temperatures by assuming that the correction will decrease with an increase in temperature as does the modulus of elasticity of columbium. Some error (0.1 psi at higher temperatures)

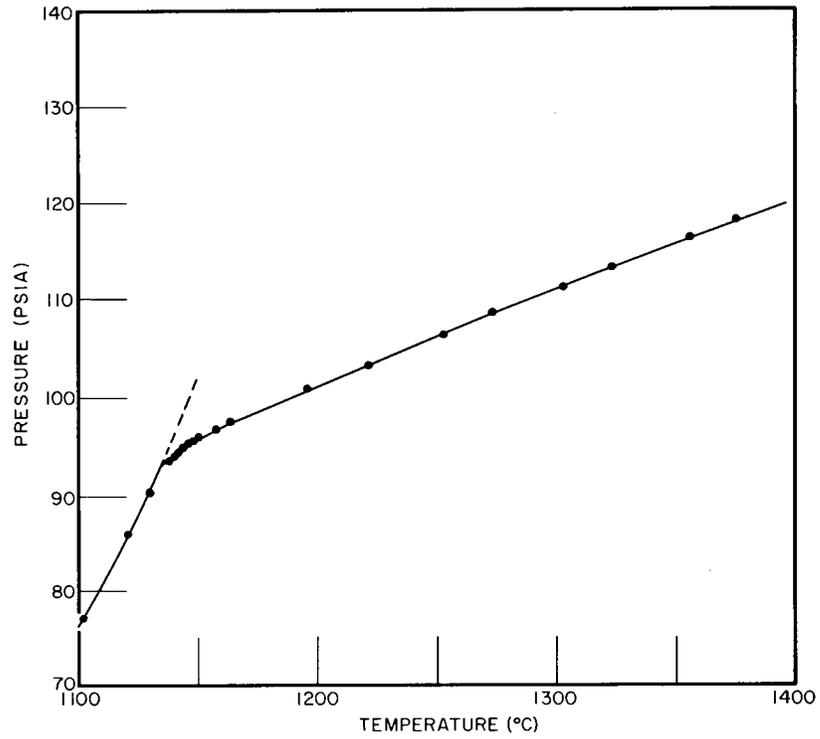


Fig. 3 - Pressure-volume-temperature data for sodium--null-point experiment no. 3

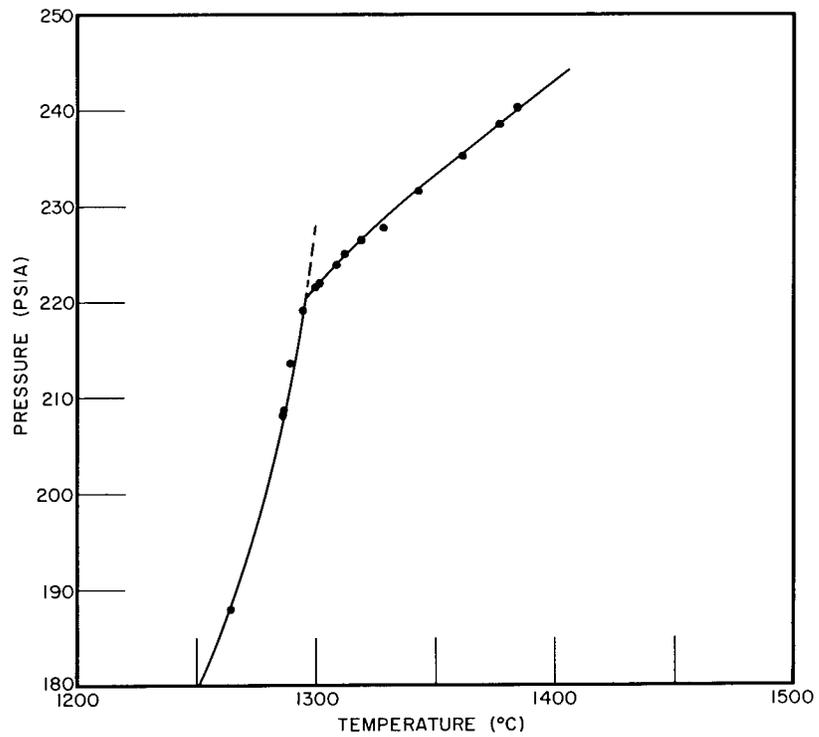


Fig. 4 - Pressure-volume-temperature data for sodium--null-point experiment no. 5

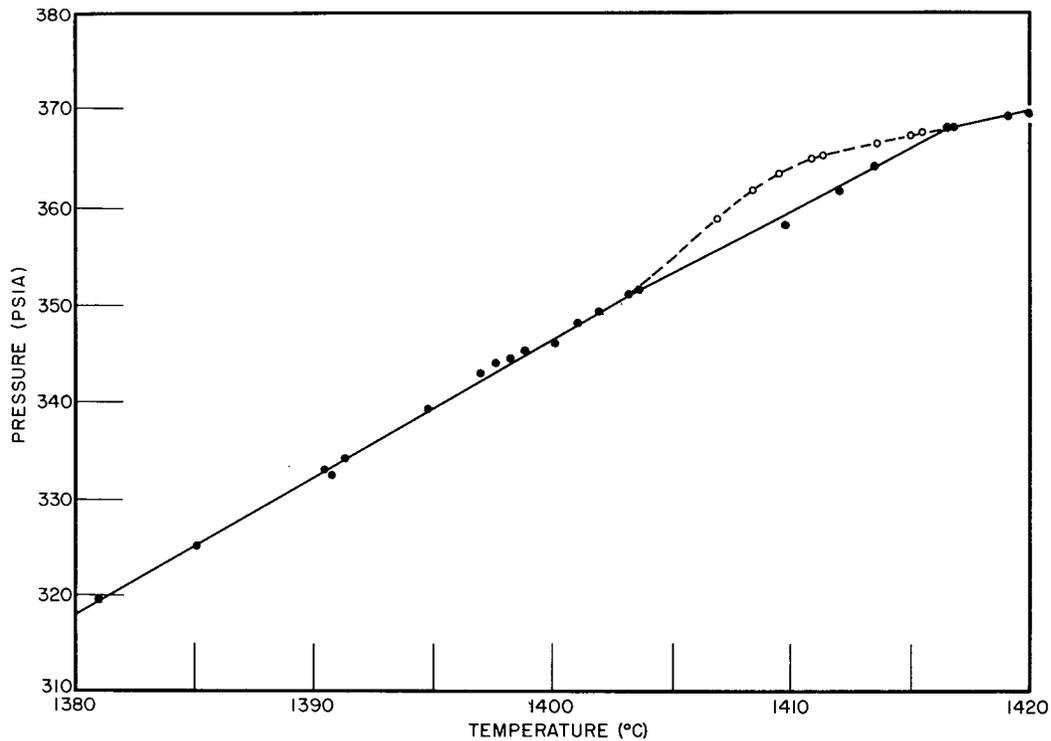


Fig. 5 - Pressure-volume-temperature data for sodium—null-point experiment no. 7

could be attributed to this assumption. Therefore, before a final treatment of the data is made, an empty apparatus will be installed in the pressure furnace with a small tube leading outside for a direct observation of the deflection pressure and its change with temperature.

Several sensitivity measurements, made on diaphragms before and after firing at 1380°C, have shown that there is effectively no change in sensitivity after the high temperature firing. The 5-mil sheet of Cb-1% Zr, from which the diaphragms were made, appeared to be fully annealed and exhibited no contamination or physical hardening upon firing. As one would suspect from the sensitivity measurements, an excellent reproducibility of diaphragm motion has been obtained consistently throughout the PVT measurements. Measurements were made over at least one full cycle from room temperature to 1380°C, and equilibrium pressures were generally reproduced to better than ± 0.1 psi before, during, and after cycling.

Temperatures were measured with two calibrated Pt-6% Rh/Pt-30% Rh thermocouples — one at each end of the null-point apparatus. All thermocouples were calibrated at NRL by direct comparison with NBS standardized couples (calibrated at the Bureau against primary melting points to the gold point 1060°C, and against optical pyrometers to 1500°C). The instability, or change in output with time, for typical measurement couples appeared to become significant after two or three cycles to 1380°C. Therefore, thermocouples are used for a maximum of three cycles and then replaced.

An isothermal condition of the null-point apparatus for an experimental determination of pressure is assured by an adjustment of the furnace heaters so that observed temperatures at the top and bottom of the apparatus are matched within 1°C. The relatively short length (3 inches) and large bulk (1/4-inch-thick walls) of the chamber assure

isothermal conditions at intermediate points. Except for pressures and temperatures near the intersection of the saturation and superheat curves, temperature differences as high as 1°C between the ends of the chamber produce no apparent error.

Pressures were observed with three precision Wallace and Tiernan gages with ranges of 0 to 50 psia, 0 to 300 psia, and 0 to 500 psia. The three gages were calibrated, in situ, with a dead weight piston gage by personnel of the Eastern Standards Laboratory. The low pressure portion of the 0 to 50 psia gage was also checked against a mercury manometer.

The procedure for introducing sodium into the null chamber has been described (3). Distilled sodium was introduced into small, tared, closed-end tubes of the columbium alloy and these tubes were inserted into the null chamber. All filling operations, which included weighing the tubes of sodium, were performed in the vacuum-inert gas box. By the use of calibrated weights and a precision Mettler balance, the observed weights of sodium are believed to be accurate within ± 0.1 mg.

Another weight measurement is obtained indirectly by an analysis for total alkali at the conclusion of each experiment. Although the precision of this analytical determination is reduced in some cases by the number of washings required for complete removal of the sodium, the weights by analysis are within 0.1 to 0.4 mg. of the observed weights. The purity of the sodium using a nickel still for distillation (4) has been determined by spectrographic tests made previously at NRL. Metal impurities are present in such low concentrations that they should not influence the vapor pressure determinations; and the sodium oxide, although present in low concentrations, should be effectively gettered by the Cb-1% Zr container. Additional tests for purity are to be made.

The exact volume of a given null-point apparatus is obtained by precise dimensioning of the chamber before and after the experiment. Volumes, obtained before and after firing, differ randomly by about 0.1%, and the experimental volume is taken as the average. Corrections for the change in volume with temperature can be accurately computed from expansion data which have been measured at NRL for Cb-1% Zr. Linear expansion of the alloy as determined with a standard sapphire dilatometer to 1400°C can be determined by the following equation:

$$L_t = L_o [1 + 6.473 \times 10^{-6} (t - 25)]$$

where L_t is the length at temperature t and L_o is the length at 25°C.

One initial problem with the null-point apparatus was the inclusion of inert gas in the chamber during the welding operation. This was solved by maintaining pressure with the pinch-off tool jaws during welding. Each null chamber is checked for gas at the conclusion of an experiment by opening the chamber to an evacuated manometer. Gas pressures as low as 0.01 psi could have been detected in this manner.

The thermodynamic quantities for a vapor with mobile equilibria present can be obtained from PVT data by the use of either of two rather different methods. In the first, the gas is treated as a mixture of stable molecular species or clusters — monomers, dimers, trimers, etc. Other thermodynamic quantities are derived from equations relating molecular composition, equilibrium constants, and enthalpies of the mobile reactions. In the second method, the gas is treated as a monatomic assembly with imperfections given by a virial equation of state, and other thermodynamic quantities are obtained as corrections to those of the monatomic gas in terms of the virial coefficients. The two methods are effectively equivalent, and the choice of methods depends principally on the type of PVT data obtained and on the degree of chemical interaction.

For the initial treatment of the sodium data, corrections will be made for small gas imperfections and the vapor will be treated as a perfect mixture of molecular species. Since three or four additional experiments are required to complete the coverage of the superheat region, only a very preliminary treatment of the data has been made. The data for the first five experiments are internally consistent and two molecular species have been identified — a dimer and a trimer.

For vapor states in the superheat region, thermodynamic treatment of the PVT data will provide the following information: mole fractions of monomer, dimer, and trimer; equilibrium constants for the dimerization and trimerization reactions; and enthalpy, entropy, free energy, and specific heat. The specific volume of the vapor in the superheat region can be calculated directly from the weight of the sodium and the volume of the chamber, and is independent of the thermodynamic treatment. Specific volume of the saturated vapor is obtained at the intersection of the saturation and superheat vapor curves. It will be noted in Figs. 2 to 5 that these intersection points, in general, are sharp and well defined.

Saturated Vapor Pressure

The vapor pressures of sodium (from 1 to 25 atm) as observed in five null-point experiments are shown in Fig. 6, where $\log p$ is plotted versus $1/T$. The slope of this curve, $d(\log p)/d(1/T)$, at any temperature is roughly related to the enthalpy of vaporization, and the observed decrease in slope (or decrease in the enthalpy of vaporization)

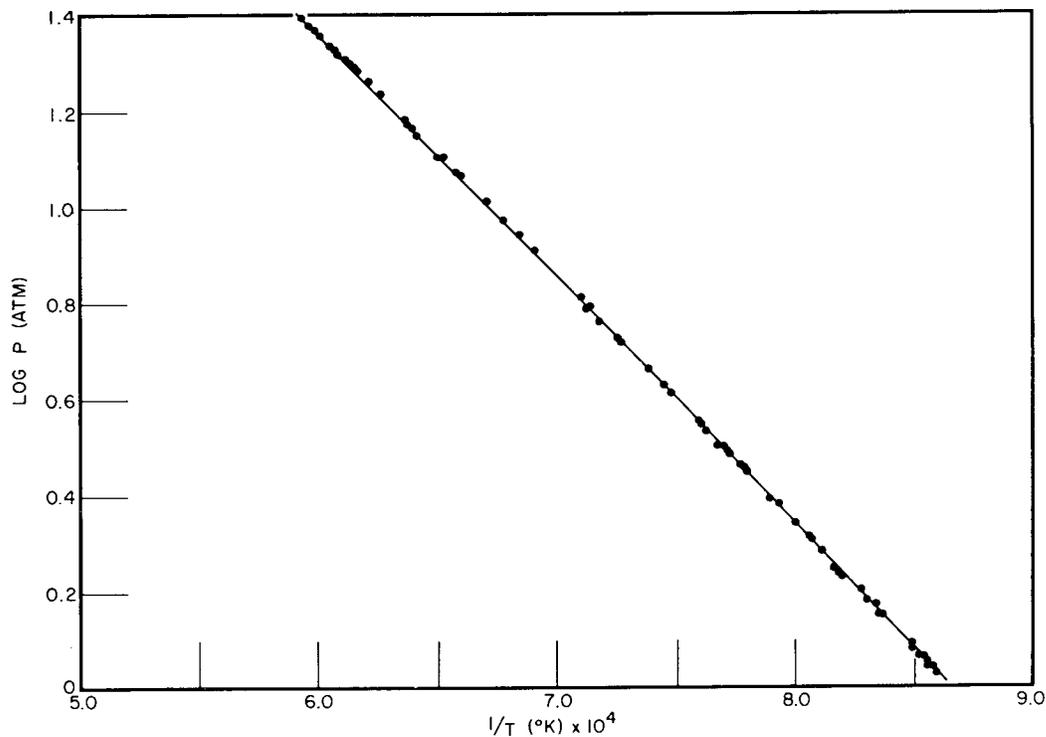


Fig. 6 - Vapor pressure of sodium

appears to be related to the rate of polymer buildup in the vapor. This behavior is consistent with other thermodynamic considerations, and it is believed that the vapor pressure data can be fitted by an equation involving the normal thermodynamic quantities, together with the rates of polymer buildup and the enthalpies of the polymerization reactions.

It is of interest to compare the observed vapor pressures with those of previous investigators. Vapor pressures of sodium above its normal boiling point have been observed by Kirillov and Grachev (5) over the pressure range of 1.2 to 15.4 atm, by Bowles and Rosenblum (6) over the pressure range of 2 to 120.4 atm, and by Makansi, et al (7) over the pressure range of 0.047 to 6.489 atm. The vapor pressure curve by Kirillov and Grachev intersects the NRL curve at both low and high temperatures, but at intermediate points it is below the NRL curve by as much as 7 psi. Vapor pressures by Bowles and Rosenblum agree with those by NRL near the normal boiling point of sodium, but they diverge widely at higher temperatures and are roughly 40 psi higher than those at NRL at temperatures near 1416°C. The vapor pressures of Makansi exhibit good agreement with those of NRL, and deviations are probably within the limits of the combined errors.

Specific Heat

Specific heats of saturated liquid sodium have been determined from 100° to 1170°C. An Inconel bucket containing the alkali metal is equilibrated at a known temperature in a specially designed furnace and dropped into the calorimeter, permitting a measurement of the heat evolved in cooling the sample to 30°C (the standard operating temperature of the calorimeter). This procedure is repeated at a number of furnace temperatures for both filled and empty buckets, and the heat capacities of the sample are derived by standard calorimetric procedures.

The heat capacities of sodium and of sapphire, a calorimetric standard material, are presented in Tables 1 and 2. Heat capacities for each material are compared to

Table 1
Specific Heat of Saturated Liquid Sodium (High Temperature System)

Temp (°C)	NRL C _p (cal/gm °C)	NBS C _p (cal/gm °C)	$\left(\frac{\text{Percent Deviation}}{\text{NBS } C_p} \right)$ $\left(\frac{\text{NRL } C_p - \text{NBS } C_p}{\text{NBS } C_p} \right)$
315.9	0.314	0.312	+0.7
599.5	0.301	0.300	+0.3
723.9	0.291	0.301	-3.3
826.4	0.297	0.304	-2.3
920.5	0.313	0.309*	+1.3
1008.9	0.324	0.316*	+2.5
1109.6	0.325	0.326*	0.0
			Mean ±1.5

*Extrapolated with NBS equation.

Table 2
Specific Heat of Sapphire (High Temperature System)

Temp (°C)	NRL C _p (cal/gm °C)	NBS C _p (cal/gm °C)	$\left(\frac{\text{Percent Deviation}}{\text{NBS } C_p} \right)$ $\left(\frac{\text{NRL } C_p - \text{NBS } C_p}{\text{NBS } C_p} \right)$
278.8	0.246	0.250	-1.6
647.5	0.279	0.286	-2.4
723.4	0.285	0.292	-2.4
824.6	0.292	0.296	-1.4
917.1	0.292	0.298*	-2.2
1009.4	0.304	0.301*	+1.2
1112.4	0.303	0.303*	0.0
			Mean ±1.6

*Extrapolated with NBS equation.

corresponding values obtained at the National Bureau of Standards (8). Comparison results for sodium above 900°C, the limit of the NBS measurements, represent an extrapolation using their specific heat equation. Although the deviations for each material are generally below ±2%, which is within the probable error of the NRL measurement (±3%), they are higher than those obtained in previous measurements on the same materials at lower temperatures. As a consequence, the method and measurement system were completely reexamined for possible sources of error. The calorimeter was recalibrated electrically; modifications were made to the furnace to minimize convection effects at the bucket during equilibration; sample thermocouples were replaced; and factors related to the bucket drop were reanalyzed. No significant error source was discovered. It is now believed that the reduced measurement precision resulted from a combination of the relatively low sample weight and the low sample-to-container, heat-content ratio of one to three which tended to magnify nominal system errors. The thick walled container, with its unfavorable heat-content ratio, was required to withstand the pressure of the sodium vapor.

Specific heats of sodium at intermediate temperatures were measured at NRL several years ago but were not published. These results are now reported in Table 3 and are, likewise, compared with corresponding NBS values. The mean deviation of this data is only ±0.5%, since the measurements were made under more favorable conditions using an iron bucket with a sample-to-container, heat-content ratio of two to one.

The specific heat results are presented graphically in Fig. 7. Below 900°C, the NBS specific heat curve (8), as computed from their equation, has been drawn through the experimental points and is shown to provide an excellent fit. Above 900°C, the points are adequately represented by an extension of the same equation. Thermodynamic considerations and the expected form of the equation for extrapolation to higher temperatures will be discussed in a later report.

Table 3
Specific Heat of Saturated Liquid Sodium (Low Temperature System)

Temp (°C)	NRL C_p (cal/gm °C)	NBS C_p (cal/gm °C)	$\left(\frac{\text{Percent Deviation}}{\text{NBS } C_p} \right)$ $\left(\frac{\text{NRL } C_p - \text{NBS } C_p}{\text{NBS } C_p} \right)$
155.2	0.325	0.325	0.0
255.3	0.315	0.315	0.0
352.0	0.312	0.308	+1.3
449.7	0.304	0.303	+0.3
555.3	0.297	0.300	-1.2
652.6	0.300	0.300	0.0
			Mean ± 0.5

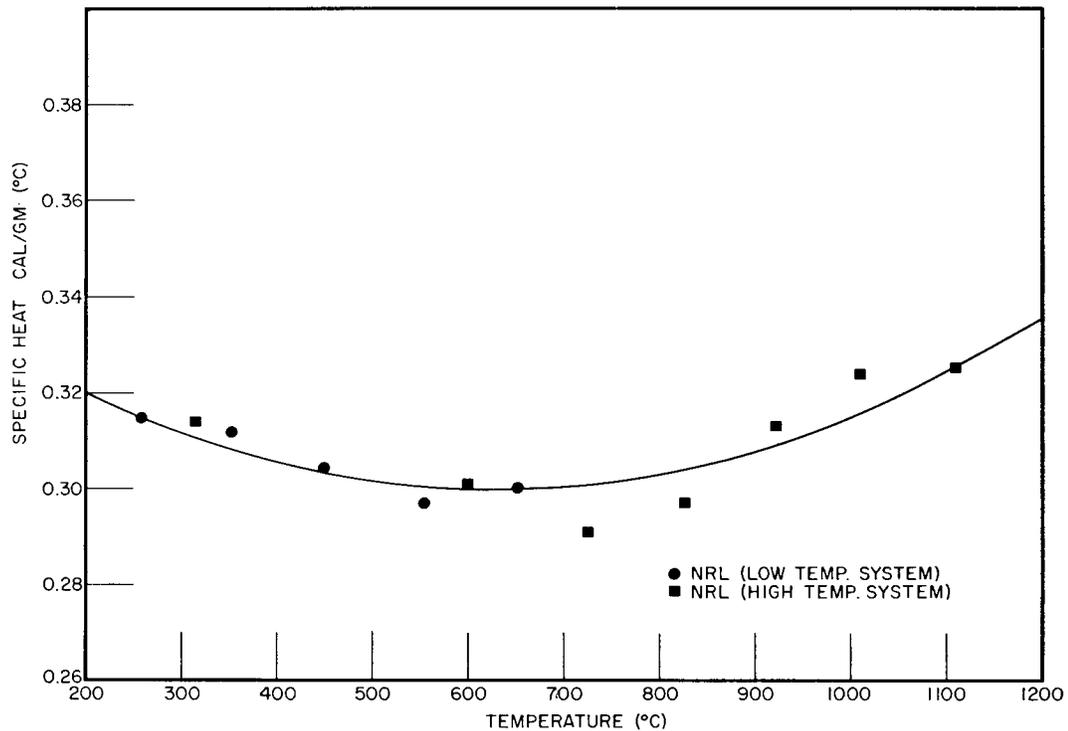


Fig. 7 - Specific heat of liquid sodium

Specific heat data for potassium will be obtained in two steps. A thick walled, Inconel container must be used at higher temperatures and pressures. However, over the low vapor pressure range from the melting point to approximately 850°C, a thin walled

container will be used for increased precision. These measurements should be completed this fiscal year.

Equilibrium Solubilities of Columbium and Zirconium in Liquid Sodium

Radioactive tracer methods were used to determine the equilibrium solubility of the Cb-1% Zr alloy in liquid sodium at elevated temperatures under static, isothermal conditions. The solubility apparatus (9), made of the alloy, was loaded with vacuum distilled and filtered sodium. The apparatus was hermetically sealed under an atmosphere of purified argon, shrouded externally with titanium foil, and assembled in the pressure furnace. The system was heated to the desired temperature as determined by a Pt/Pt-10% Rh thermocouple and the sodium allowed to come to equilibrium with the container for a period of eight hours. The sodium was sampled into a molybdenum receptacle at the equilibrium temperature by 180 degree rotation of the apparatus. Upon cooling of the system to room temperature, the solubility apparatus was removed, opened near the bottom of the sampling compartment, and the sample in the molybdenum crucible analyzed for columbium and zirconium.

The analytical scheme (10) for the sample entailed a separation of the dissolved columbium and zirconium from an aqueous sodium solution by a nonisotopic carrier technique. Approximately 10 mg of iron scavenger were used. Due to the unique nuclear characteristics of columbium-94m, one milligram deposits of the scavenger as Fe_2O_3 of uniform surface density (0.26 mg/cm^2) were irradiated in the NRL reactor for 15 minutes and analyzed by the standard comparator technique for columbium. Columbium concentrations were determined radiometrically by an x-ray detector in conjunction with a filtering technique to screen out interfering, extraneous beta activity. Resolution of composite decay curves revealed mostly a 6.6-minute half-life activity characteristic of columbium-94m. The remainder of the scavenger (approximately 9 mg of iron as Fe_2O_3) was irradiated for one hour and also analyzed by the standard comparator technique for zirconium. The characteristic zirconium-97 activity was separated radiochemically from the scavenger by an isotopic carrier technique, purified, and its activity counted beta-wise in conjunction with a filtering technique to screen out the long-lived zirconium-95 activity. Counting of the zirconium-97 activity was started after sufficient time had elapsed for the columbium-97 daughter activity to come to equilibrium. The resultant activity decayed with a 17-hour half-life characteristic of zirconium-97.

The results of the solubility experiments are compiled in Table 4. The data indicate that equilibrium conditions were established within eight hours.

Table 4
Equilibrium Solubility of Cb-1% Zr in Liquid Sodium

Temp. (°F)	Cb Solubility (p.p.m.)	Zr Solubility (p.p.m.)	Equilibration Time (Hours)
1475	178	1.72	2
2165	12	2.40	2
1477	17.9	0.77	8
1846	7.5	0.57	8
2158	35.2	0.97	8
2516	243.0	3.60	8

Semilog plots of the concentrations of columbium and zirconium versus the reciprocal of the absolute temperature for eight-hour equilibrations are shown in Fig. 8. The solubilities of both constituents as determined by the low temperature experiments appear to be about a factor of ten times too high to be internally consistent with the higher

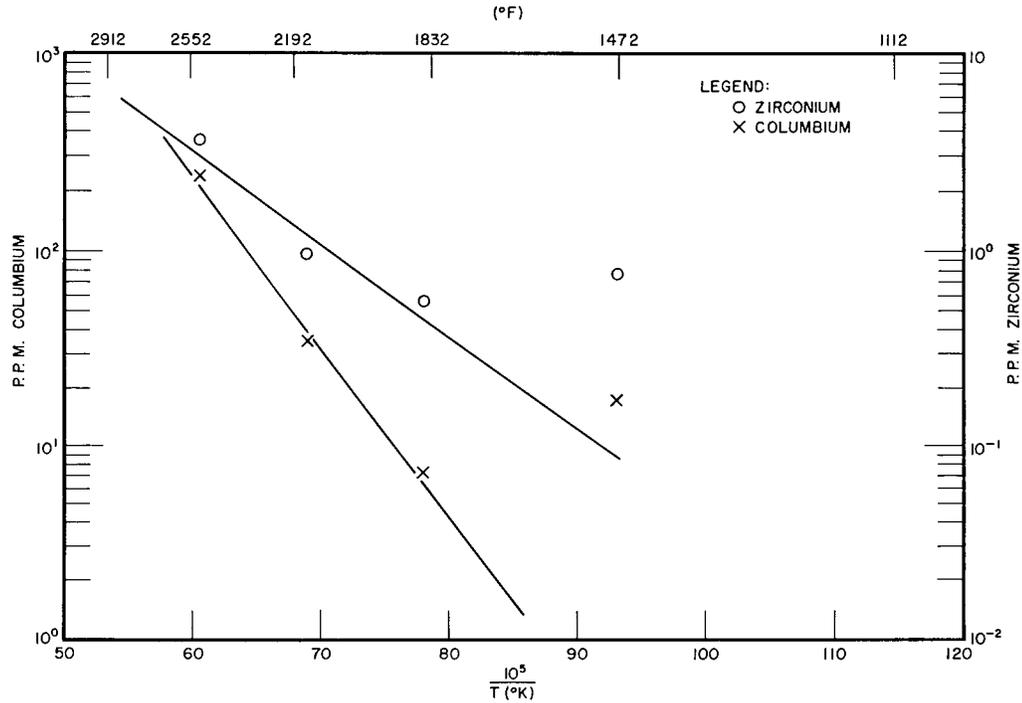


Fig. 8 - Solubility of Cb-1% Zr alloy in sodium

temperature values. These discrepancies and the poor precision of the solubility values, in general, can possibly be attributed to unknown impurity parameters. The level of the minor contaminants in the equilibrating sodium, particularly the oxide and hydroxide, needed to be established to determine their significance in the solubility results. However, attempts to sample the sodium without additional contamination for impurity analyses at the end of a particular experiment were unsuccessful.

REFERENCES

1. Stone, J. P., Ewing, C. T., Spann, J. R., Steinkuller, E. W., Kovacina, T. A., and Miller, R. R., "High Temperature Properties of Sodium—Sixth Progress Report 1 January to 31 March 1962," NRL Memo Report 1312, Apr. 1962
2. Ewing, C. T., Stone, J. P., Spann, J. R., Steinkuller, E. W., Kovacina, T. A., and Miller, R. R., High Temperature Properties of Sodium and Potassium—Seventh Progress Report for Period 1 April to 30 June 1962, NRL Report 5844, Aug. 1962
3. Ewing, C. T., Stone, J. P., Spann, J. R., Kovacina, T. A., and Miller, R. R., "High Temperature Properties of Sodium—Fifth Progress Report for Period 1 Oct. to 31 Dec. 1961," NRL Memo Report 1263, Jan. 1962
4. Ewing, C. T., and Grand, J. A., "Measurements of the Thermal Conductivity of Sodium and Potassium," NRL Report 3835, Aug. 1951
5. Kirillov, P. L., and Grachev, N. J., Grachev, Inzh. Fiz. Zhur., Akad. Novk Belorussk. SSR 2:3 (1959)
6. Bowles, K., and Rosenblum, L., Report E-1426, Lewis Research Center, NASA, Cleveland, Ohio. Presented as Paper No. 27, 54th Annual Meeting, Amer. Inst. of Chem. Engrs. (Dec. 5, 1961)
7. Makansi, M. M., Muendel, C. H., and Selke, W. A., J. Phys. Chem. 59:40 (1955)
8. Ginnings, D. C., Douglas, T. B., and Ball, A. F., J. Res. Nat. Bur. St. 45:23 (1950)
9. Ewing, C. T., Stone, J. P., Spann, J. R., Kovacina, T. A., and Miller, R. R., "High Temperature Properties of Sodium—Fourth Progress Report for Period 1 April to 30 Sept. 1961," NRL Memo Report 1236, Oct. 1961
10. Kovacina, T. A., "Sodium Liquid- and Vapor-Phase Corrosion Studies at High Temperature Using Radiochemical Methods," presented at NASA-AEC Liquid-Metals Corrosion Meeting, Dec. 7-8, 1960, NASA TN D-769, pp. 73-74, Wash., D. C., Feb. 1961