

AD625902

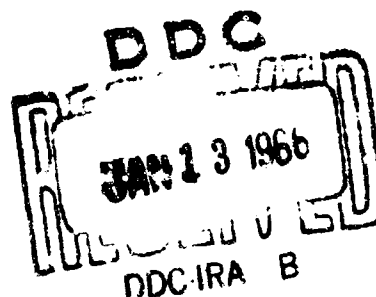
# HIGH TEMPERATURE PROPERTIES OF SODIUM FIFTH PROGRESS REPORT FOR PERIOD 1 OCTOBER TO 31 DECEMBER 1961

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

CHEMISTRY DIVISION

CLEARINGHOUSE FOR FEDERAL SCIENTIFIC AND TECHNICAL INFORMATION			
Hardcopy	Microfilm		
\$1.00	\$6.50	10	20
ARCHIVE COPY			

Code:



January 1962

PROCESSING COPY

Distribution of this document  
is unlimited.



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

~~Further distribution of this report, or of an abstract,  
or reproduction of any part of the report, is authorized  
only by the U. S. Naval Research Laboratory,  
Washington, D. C. 20340, or by the activity sponsoring  
the research reported therein, as appropriate.~~

NRL Memorandum Report 1264

HIGH TEMPERATURE PROPERTIES OF SODIUM

Fifth Progress Report  
For Period 1 October to 31 December 1961

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

Inorganic and Nuclear Chemistry Branch  
Chemistry Division

January 1962

U. S. NAVAL RESEARCH LABORATORY  
Washington 25, D. C.

## CONTENTS

ABSTRACT	ii
PROBLEM STATUS	ii
AUTHORIZATION	ii
INTRODUCTION	1
EXPERIMENTAL PROGRAM	1
INDIVIDUAL PROPERTY TESTS	2
Pressure-Volume-Temperature	2
Density	3
Specific Heat	4
Equilibrium Liquid Solubilities	4
Condensing-Vapor Corrosion	6
REFERENCES	6

## ABSTRACT

An experimental program has been established at NRL to measure thermophysical properties of sodium and sodium vapor to 2500°F. The status of the various property measurements and some of the problem areas encountered at these temperatures are discussed.

## PROBLEM STATUS

This is a preliminary report on the problem; work is continuing.

## AUTHORIZATION

NRL Problem C05-15  
NASA Order Number NTF-92

## HIGH TEMPERATURE PROPERTIES OF SODIUM

Fifth Progress Report  
For Period 1 October to 31 December 1961

### INTRODUCTION

Turboelectric systems utilizing a metal vapor as the working fluid are attractive for space missions requiring electric power. Several metals are of interest as working fluids: mercury, rubidium, potassium, sodium, and lithium. The National Aeronautics and Space Administration is supporting the Laboratory's effort to evaluate thermodynamic and transport properties of sodium to 2500°F.

### EXPERIMENTAL PROGRAM

The present sodium program includes the measurement of vapor pressure, P-V-T properties, density (vapor and liquid), specific heat (liquid), and radiochemical studies to determine equilibrium solubilities and condensing-vapor corrosion of container metals (columbium and zirconium). The property measurements should provide, directly or by calculation, all of the thermodynamic entities required to compile accurate temperature-entropy and enthalpy-entropy diagrams for sodium.

Three high pressure furnaces and their sub-assemblies have been described in detail in a previous report (ref. 1). Difficulty was experienced in obtaining a positive seal between the inner chamber and the furnace proper for both upright furnaces. However, modified silver chloride seals have now been installed in the furnaces and have provided positive closures. All three furnaces have been used to heat columbium apparatuses and have provided the required protection against embrittlement of the material by trace contaminants.

Cover gas for protection of the columbium alloy is supplied by passing welding-grade argon through pressurized trains of molecular sieve and hot titanium sponge (1500° to 1700°F). The oxygen content of the purified gas, monitored by an electrolytic analyzer (ref. 1), has been consistently lower than 1 ppm.

All welding operations are being performed in a large, inert gas box. The glove ports on this box are being modified to take polyvinylchloride gloves with 8 inch seals, since gloves with 5 inch seals are no longer available. However, welding and filling operations are continuing with standard rubber gloves.

## INDIVIDUAL PROPERTY TESTS

### Pressure-Volume-Temperature

A null point method will be used to provide enthalpies, entropies, specific volumes and dimerization data for vapor states in the superheat region. Although two types of apparatuses (ref. 2) are to be used, both are closed chambers machined from the columbium alloy and equipped with flexible diaphragms. The diaphragm is maintained at a fixed position by a balance of the external and internal pressure so that the measurement of sodium pressure is made externally with calibrated Bourdon gages.

Design requirements for a diaphragm of the columbium alloy to operate effectively at temperatures to 2500°F were not definitely known. From rough calculations, based on estimated mechanical properties, a diaphragm with a thickness of 5 mils and a free diameter of 1.5 inches was selected. A simple apparatus, designed for visual observation of diaphragm movement, was made specifically for the preliminary testing of diaphragms. This apparatus was assembled with a diaphragm, closed under one atmosphere of argon, positioned in the quartz tube of the pressure furnace, and heated slowly up to 2000°F. Visual observation of diaphragm movement was possible only to 1500°F at which time metal vapors (titanium and molybdenum) condensed on the walls of the quartz tube. However, an observation of movement after firing was obtained upon removal of the apparatus from the furnace. The observed reproducibility of measured pressures was in the range of  $\pm 0.1$  psi before and after firing. Pressure sensitivity (in this case the pressure differential required for full diaphragm deflection) after firing was below 0.2 psi.

An apparatus, designed for electrical pick up of diaphragm movement, will be used for the P-V-T studies of sodium. The first apparatus of this type, when assembled and welded,

exhibited an "oil-canning" of the diaphragm, and a differential pressure of 2.5 psi was required for full deflection. This condition was corrected by modifying the welding operations, and no "oil-canning" was observed with the rewelded diaphragm, which had a pressure sensitivity below 0.1 psi.

The procedure for charging the null apparatus with sodium has been modified. Distilled sodium will be introduced into small, tared, closed-end tubes of columbium alloy and these tubes introduced into the null apparatus through the filling port. All filling operations, including weighing the tubes of sodium, will be performed in the vacuum-inert gas box. After sodium is introduced, the closure tube permits a thorough degassing and evacuation of the chamber before the tube is closed by welding. Immediately prior to the final filling operation, a thorough degassing of the apparatus at 1650°F will have been performed.

Degassing and filling operations for the first null apparatus should begin about the 15th of January and P-V-T measurements should follow about the 1st of February.

### Density

Density of sodium will be determined point-wise with small pycnometers (ref. 2) of columbium alloy. The density will be obtained directly by weighing the sodium remaining in the calibrated volume after equilibration at a given temperature, and indirectly by chemical analysis for total alkali of the metal removed from the chamber.

The first density experiment was made at approximately 2100°F with a pycnometer operated under vacuum as a closed system. This experiment was unsuccessful as only a few grams of sodium remained in the pycnometer chamber; the bulk of the metal had flash-distilled to the upper reservoir. Two thermocouples were attached at the top and bottom of the apparatus to permit adjustment to isothermal conditions. At some time during the run, metal vapors (titanium and molybdenum) had condensed on the thermocouple insulation several inches above the apparatus shorting the couple wires at sheathing junctions. The subsequent incorrect thermocouple readings prevented a proper adjustment of furnace heaters which undoubtedly led to thermal gradients along the axis of the apparatus. This condition in future experiments will be avoided by the use of full length sheathing for all couples.

An analysis of the method disclosed the possibility of flashing vapor from the pycnometer to the upper reservoir as the apparatus is reduced in temperature from equilibrium run conditions. The amount of sodium remaining in the pycnometer normally exceeds that in the reservoir; the heat liberated by this excess sodium results in a non-isothermal condition which could adjust itself by a flashing of the sodium to the upper reservoir.

To prevent the possibility of distilling metal from either chamber to the other, future apparatuses will be operated under an externally applied pressure of argon exceeding the vapor pressure of sodium at all temperatures. Only minor modifications to the pycnometer and the flange at the top of the furnace to permit pressurization are required.

The first density experiment with the new apparatus should be made around the 15th of January.

#### Specific Heat

Heat contents and specific heats of sodium to 2200°F will be measured by a drop-method (Inconel buckets) and a copper-block calorimeter (ref. 3).

Difficulty has been experienced with the calorimeter system, and observed results for sodium and sapphire at lower temperatures do not check results for these materials measured previously at this Laboratory. The calorimeter has been recalibrated electrically, and modifications have been made to the furnace to eliminate the possibility of convection effects at the bucket during equilibration. The specific heat measurements are being subordinated to the more important phases of the program, but additional heat content measurements for sodium with the modified furnace will be made as time permits.

#### Equilibrium Liquid Solubilities

The radiochemical work to determine the equilibrium solubility of the columbium-1% zirconium alloy in high temperature sodium has progressed with the completion of two additional runs at temperatures of 2500° and 2150°F. As a result of these experiments, some difficulties have been discovered



and a few remedial changes of a minor nature are being made in both the design of the equilibration apparatus and also the operating conditions of the experiments. The ensuing account of the aforementioned runs will tend to illustrate these problem areas and the corrective measures being taken.

For the experiment at 2500°F, sodium was equilibrated at temperature for two hours and was sampled as previously described (ref. 3). Upon opening the equilibration vessel it was found that 7.7 grams of sodium was recovered in the graphite sampling crucible while 8.64 grams was held up in the equilibration chamber. An increased sampling yield is desirable to obtain the required analytical sensitivity, especially if solubilities are found to be low.

One explanation for the hold up of sodium in the equilibration chamber (the top chamber while sampling) would be the adherence of sodium around the lower wall in the form of a broad concave meniscus. Sodium menisci with curvatures sufficient to have caused the observed hold up have been noted previously in stainless steel tubes of comparable diameters. This condition should be corrected by the addition of an off-center port between the two chambers.

A preliminary chemical analysis of the sodium sample from the experiment at 2500°F indicated the presence of macro amounts of columbium and zirconium. The metal contents are higher than would be expected for pure solubility and could be attributed to a number of reasons. One might be a mechanical abrasion of oxidized surfaces of the alloy and subsequent entrainment of particulate oxide in the sodium during the sampling procedure. Particulate metal might also be built up in the sodium prior to sampling by a refluxing mechanism if non-isothermal conditions exist along the apparatus. Either of these phenomena, if found to be present, will necessitate a sampling of the sodium through a porous disc of the columbium alloy.

Another explanation for the high analytical values might be a refluxing of the sodium off the walls of the vessel after the sampling step. This condition could occur upon cooling the furnace by the same mechanism described for the density experiments. As an immediate solution to the problem of possible refluxing, future experiments will be made with the sodium under argon pressure, rather than a vacuum. Facilities for the rapid cooling of the sodium-containing portions of the

apparatus immediately after sampling will be considered if refluxing is evident in further tests.

The experiment at 2150°F was only partially successful for reasons similar to those already described. In this case, the sample crucible contained only 2.5 grams of sodium with the bulk again being held up in the equilibration part of the apparatus.

#### Condensing-Vapor Corrosion

This phase of the radiochemical study will follow the liquid solubility work, and detailed design of apparatus has not been finalized.

#### REFERENCES

1. C. T. Ewing, J. P. Stone, J. R. Spann, T. A. Kovacina, and R. R. Miller, NRL Memo Report 1165, 10 May 1961.
2. C. T. Ewing, J. P. Stone, J. R. Spann, T. A. Kovacina, and R. R. Miller, NRL Memo Report 1236, 6 Oct 1961.
3. B. E. Walker and C. T. Ewing, WADC Technical Report 54-185, Part I, July 1954.