NOTICE

Need ERDA-427

Technical Progress Report has been reproduced from the best available copy to permit the broadest possible availability.

to the

Materials Sciences Program
Division of Physical Research
U.S. Energy Research & Development Administration

of work on

"High Temperature Properties of Nuclear Reactor
Coolants and Thermodynamic Power Cycle Working Fluids"

under contract

E(11-1) - 3027

MASTER

for the period

October 1 '74 - Sept. 30 '75

Charles F. Bonilla - Principal Investigator
Liquid Metals Research Laboratory
Dept. of Chemical Engineering & Applied Chemistry
Columbia University
New York, N.Y. 10027

August, 1975

NOTICE

PORTIONS OF THIS REPORT ARE ILLEGIBLE. It has been reproduced from the best available copy to permit the broadest possible availability.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *ek*

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

High Temperature Properties of Nuclear Reactor
Coolants and Thermodynamic Power Cycle Working Fluids

A. Abstract

During this contract year, vapor pressure measurements on sodium by the Pressure Tube method were obtained up to 3,267 lbs/sq.in. absolute and 4340 deg. Rankine, which is more than double the maximum pressure previously reached by others. The critical point has not yet been reached, but the above values do provide a lower limit to the critical point. This information may be useful in some situations until the actual data are obtained in subsequent runs with improved equipment.

A picnometer-type apparatus for measuring the isothermal compressibility of liquid sodium has been completed. It was tested with water, giving reasonably good checks of Steam Table values. This apparatus is expected to be able to also provide P-V-T data on sodium up to some 3000 F, and on cesium to the critical region.

The program on properties of mercury vapor to high pressures was completed with its thermal conductivity to 3000 lbs/sq.in. abs. and up to 80°C of superheat. Preliminary analysis yields data which agree within 7%, or 20°C, with previous results from this laboratory up to atmospheric pressure.

A NaK and sodium loop with capacities of approximately 5 gallons per minute, 40 lbs/sq.in. pressure drop and over 1200°F has been reconditioned and installed to be available for LMFBR and similar tests and programs.

B. HIGH TEMPERATURE VAPOR PRESSURE OF SODIUM
(Preliminary Results)

1. "Pressure - Tube" Method

The vapor pressure of sodium was measured experimentally in July/August 1975 over the temperature range of 2200-3900°F, using the "pressure-tube" method originated in this laboratory and used successfully to measure the vapor pressures and critical points of cesium, rubidium and potassium. In this first test with sodium at the highest temperature some sodium leakage developed.

In this technique, the liquid metal is charged into a thick-walled, narrow-bore, closed-end tube made of refractory metal capable of withstanding the temperatures and pressures involved. At the open end, the pressure-tube is connected to pressure gauges and transducers using high-pressure S.S. tubing. Enough liquid metal is charged to completely fill the pressure-tube and to partially fill the connecting S.S. tubing. The remaining space is filled with dodecane (any non-reactive oil stable to 400°F is adequate). The pressure-tube is then inserted into a furnace through a gas-tight seal, so that, upon heating, in the temperature range involved, the closed end tip is at the highest temperature along the pressure tube with a continuously negative temperature gradient away from the tip. The tube is then heated so that an alkali metal vapor bubble forms at the tip. A valve stem is now used as an injector to compress this closed system so that the vapor-liquid interface is pushed towards the closed tip. The interface encounters steadily increasing temperatures and the pressure rises correspondingly. When the interface reaches the tip, there is only liquid phase left in the system and further compression causes the rate of pressure increase to rise sharply. If the system pressure is plotted against turns of the injector stem, a sharp discontinuity (break) is observed in the curve, corresponding to the vapor pressure (with head correction) at the tip temperature. Since it is necessary to measure only the tube tip temperature, it is possible to attach a number of thermocouples there, and increase the reliability of the tip temperature determination.

As the tip temperature approaches the critical temperature, the break in the curve at the corresponding vapor pressure, continues to increase in pressure and to be sharp. However, once the tip exceeds the critical temperature, it is found

that the pressure breaks decrease in sharpness, and remain always at or near the same pressure, rather than continuing to rise in pressure. This peak value of break point pressure is the critical pressure. The explanation for a pressure break being observed with the tip temperature either below or above the critical temperature is that in either case when the critical pressure is reached, the system changes from a 2-phase to a one-phase system, which is cause enough for a break to occur at that particular pressure.

2. Experimental Set-up

For this sodium vapor pressure program the pressure tube was of CVD tungsten, 0.34 in. OD, 0.06 in. ID, and 12 in. long. The tube tip was ringed by 3 W-Re thermocouples made of Hoskins factory-calibrated wire. A tungsten-mesh furnace filled with argon at slightly above atmospheric pressure was employed. A simplified schematic drawing of the equipment is shown in Fig. 1.

The steady data recorded for each run were: tip temperature EMFs and furnace amperes and volts. In addition, some 20 increments of injector angle were employed in each run. and the linear valve stem insertion & the system pressure by a transducer were recorded by an X-Y plotter to give an immediate approximate indication of each break-point. The thermocouple EMFs were printed out every increment of injector stem insertion to correct for any tip temperature fluctuations.

A complete description of the equipment and procedure will be provided in a topical report and publication of the complete final sodium vapor and critical pressure results. The highest break point is shown in Fig. 2, indicating the excellent sharpness of break continuing to be obtained at high temperatures.

3. Experimental Results

All of the experimental breakpoints are listed in Table 1. Run 1 had produced the 7 points first given when at about 2700F a thermocouple wire touched the heater element, grounding it and damaging the thermocouple system. The thermocouples were replaced and the tests continued subsequently over a 2-day period, with partial shut-down overnight in between. The first day is designated Run 2A and the second Run 2B.

Fig. 1. Sodium Vapor Pressure Apparatus

COEFFICIENTS C(1)....C(4) ARE=
0.13020411606084960 02

-0.21459650585183170 02; LN P_{psia} = 1.30204116 - $\frac{21459.65}{T_{OR}}$

DEG-F	P OBSERVED	P CALCULATED	DIFF (PSIA)	% DIFF	
2248.81	162.30	163.58	-1.28	-0.79	1
2307.98	192.50	193.77	-1.27	-0.66	2
2367.95	220.00	228.40	-0.40	-0.18	3
2425.19	264.70	265.52	-0.82	-0.31	4
2506.60	320.30	325.66	-5.36	-1.67	5
2595.02	397.60	401.52	-3.92	-0.99	6
2679.74	456.10	444.36	11.74	2.57	7
2720.65	526.70	529.94	-3.24	-0.62	8
2793.97	617.90	616.98	0.92	0.15	9
2883.80	731.70	736.59	-4.89	-0.67	10
2930.02	831.40	803.96	27.44	3.30	11
3020.01	933.50	946.98	-13.48	-1.44	12
3061.18	1042.70	1017.79	24.91	2.39	13
3098.00	1141.70	1084.06	57.64	5.05	14
3141.38	1241.50	1165.77	75.73	6.10	15
3221.27	1323.80	1326.73	-2.93	-0.22	16
3290.95	1475.30	1478.50	-3.20	-0.22	17
3328.35	1537.60	1564.43	-26.83	-1.74	18
3390.39	1642.30	1713.96	-71.66	-4.36	19
3411.26	1724.60	1766.25	-41.65	-2.42	20
3471.04	1836.00	1921.63	-85.63	-4.67	21
3528.80	2098.80	2079.72	19.08	0.91	22
3629.40	2299.20	2374.07	-74.87	-3.26	23
3125.15	1183.30	1134.74	48.56	4.10	24
3294.04	1455.70	1485.48	-29.78	-2.05	25
3437.21	1709.90	1832.67	-122.77	-7.18	26
3511.06	1942.30	2030.33	-88.03	-4.53	27
3603.35	2150.10	2295.51	-145.41	-6.76	28
3660.56	2553.30	2470.19	83.11	3.26	29
3784.11	2939.40	2874.64	64.76	2.20	30
3789.97	2967.30	2894.75	72.55	2.44	31
3832.50	3045.20	3043.28	1.92	0.06	32
3844.47	3123.50	3085.89	37.61	1.21	33
3859.05	3205.30	3138.27	67.03	2.09	34
3879.60	3267.20	3213.00	54.20	1.66	35

RUN No. 1.
(7/75)

RUN No. 2A.
(8/75)

RUN No. 2B.
(8/75)

FROM
POWER

STANDARD DEVIATIONS OF FIT = 54.47 PSI (FROM P VALUES); 3.01 % (FROM LN P VALUES).

TABLE I. EXPERIMENTAL RESULTS ON HIGH VAPOR PRESSURE OF SODIUM.

In Run 2B, at a temperature in the neighborhood of 3800F, the thermocouples failed again. It was later observed that the W-Re wires, the MgO insulating sleeves, and a number of sheet tantalum radiation reflectors had practically evaporated or melted, presumably again because of a ground or short, or reaction between the MgO and Ta.

However 5 additional breaks were carried out. Although tip temperature could not be measured directly, it could be approximated by plotting the prior points as tip temperature vs. furnace power, and extrapolating somewhat to the furnace power of the last 5 points. Furthermore, the break point plots continued to give the vapor pressure even if their tip temperatures were not known directly, and if the critical pressure had been reached in two or more points it could have been identified by the constancy of the break point. All of the points are shown in Figure 3. It is seen that although somewhat erratic values seem to be obtained at the high temperatures (e.g. above some 3200 F) the average locus of all of the points is on, or very close to, a single straight line when plotted as $\log P$ vs $1/T$. This result is entirely in agreement with our earlier findings for potassium completely up to its critical point (1), though cesium and rubidium showed some curvature. The linear regression fit is:

$$\ln P \text{ (psia)} = 13.0204116 - \frac{21459.65}{T(^{\circ}\text{R})} \quad (1)$$

with a $\ln P$ standard deviation of 3.0% of P .

Figure 4 is a plot of the deviation of the individual points from Equation 1. Rather good agreement is seen between Runs 2A and 2B, though both are relatively erratic with respect to equation 1. The prior results of Ewing et al (2) to 2500 F and of Bowles (3) to 3300 F are also shown. Clearly the agreement is somewhat better with the former, but the new data show a surprisingly high scatter, particularly over the range of 3100 to 3700 F. It is intended to continue this study of the vapor pressure of sodium until the critical point is clearly identified and high temperature data are obtained with a substantially lower standard deviation.

Although there is no indication of reaching or approaching the critical pressure or temperature of sodium in these results to date, some information on the critical point is obtained; namely P_c and T_c are higher than the highest point

FIGURE 3. HIGH-TEMPERATURE VAPOR PRESSURE
OF SODIUM 2700 - 3900°F

obtained in Run 2. We may compare that point with our earlier straight-line extrapolations in log-log plots against atomic number from the Cs, Rb and K data (4).

	<u>P, lbs/in² abs.</u>	<u>T, deg. Rankine</u>
Critical point of Na, by extrapolation vs. atomic number (4)	2,800	4,350
Highest vapor pressure point on Na, Run 2B.	3,267	4,340

4. Conclusions

Since the previous estimates have been fairly widely used, lacking other more direct data, it may be some reassurance to point out that T_c , when actually determined, may be close to the previous estimate, up to substantially higher, and that P_c is definitely somewhat higher than the previous estimate, but that neither value is lower than the previous estimate.

Furthermore, equation 1 may be used with considerable confidence for vapor pressure over the whole pressure range. At the highest pressures it is the only equation based on actual data, and it lies between the extrapolations of the other two sources, and at lower pressures it is based on data which show very good consistency, and lie close to the other sources.

5. Bibliography

1. W.R. Jerez, V.S. Bhise, S.D. Gupta, and C.F. Bonilla "The High Temperature Vapor Pressure and the Critical Point of Potassium." Proc. of the 6th Symp. on Thermophysical Properties. Amer. Soc. of Mech. Engrs., Atlanta, Georgia, p. 353-361 (August 6-8, 1973).
2. J.P. Stone, C.T. Ewing, et. al., "High Temperature Properties of sodium," NRL Report 6241 (Sept. 24, 1965)
3. K.J. Bowles and L. Rosenblum., "Vapor Pressure of Sodium from 0.5 to 120 Atmospheres," NASA TN D-2849, Lewis Research Center, Cleveland, Ohio (May 1965)
4. C.F. Bonilla "Proposed Technical Program, AT(11-1) 3027, for 10/1/73 - 9/30/74", Submitted to Division of Research, USAEC (1973)

C. Liquid Density and Compressibility Determination

1. Introduction

A new apparatus for the determination of subcooled thermodynamic properties of liquids, particularly of sodium, was completed and tested with water. The final set-up is shown in Fig. 5.

2. Description of Apparatus

The apparatus basically consists of (1) the test liquid (e.g. sodium) system and, (2) the pressure liquid (e.g. dodecane) system. Sodium alone will not be used because packings recommended for all-alkali metal service had very low cycle life at maximum pressure-ratings (e.g. 2500 psia) at the melting point. Thus a two-liquid system, as in our vapor-pressure measurements, using dodecane, was chosen. Fig. 5 shows the separate alkali metal and oil charging arrangements. The oil-alkali metal interface is maintained during the experiments in a large S.S. tube, H, directly under the injector, to minimize its motion. All other tubing is of small ID (.027" ID) to minimize volume and compressibility external to the capsule. Two pressure transducers (2500 psig and 5000 psig ratings) record the pressure. A "Heise" Bourdon gauge is used to occasionally check their calibration. The injector is a needle valve with a 0.375" stem (the largest found) packed with Teflon and rated to over 5000 psig. An LVDT is mounted coaxially with the injector stem to measure its displacement. Pressure vs. displacement are plotted "on-line" on an x-y plotter, though all the data, i.e. pressure, displacement, temperature and time, are also recorded by an automatic data acquisition system. Alkali metal is withdrawn or added through valve B and dodecane through valve C.

3. Experimental Procedure

The normal operating arrangement is with valves B, C, D and F closed. The temperature is set and the injector stem withdrawn, as required, decreasing the pressure and allowing a vapor space to form in the bulb. Hereafter the principal operations are carried out by adjusting the vapor-liquid interface in the bulb by manipulating the injector stem and valves A, B, C. When the temperature is steady, the data acquisition system (DAS) is activated to record temperature, pressure and LVDT output.

Liquid is now cycled into and out of the bulb by the injector stem, and a record of system pressure during the run vs. stem displacement is obtained on the x-y plotter or DAS. Valve A is now closed and the test repeated to obtain the correction for external system compression. The temperature is then increased (or decreased) to a new value.

FIGURE 5.

LAYOUT OF HIGH PRESSURE-HIGH TEMPERATURE
"PICNOMETER-TYPE" OF P-V-T AND LIQUID COMPRESSIBILITY APPARATUS.

Fig. 6 is a plot of the raw data for a typical day's runs, made with water on 5/21/75, at successively higher temperatures. Water was used for verification and calibration of the system for convenience, as well as the high accuracy of its data.

4. Operational Modes

So far, three different operating techniques for obtaining different data on the fluid tested have been developed. In brief, the procedures and the results of water runs are as follows:

a) Liquid Phase Compressibilities

Initially, the contained volume of the capsule was measured separately by the volume of water admitted after evacuation to a skeleton system, both with the capsule in place and with it replaced by a solid plug, and found to be 8.142 cc. with a standard deviation of 0.05%.

Starting with the system in any condition, and only valve A open, liquid is added by the injector. If pressure does not rise, evidently vapor space is being filled with the liquid. Continuing the transfer of liquid, eventually a sudden, rapid rise in pressure is observed, such as the steep rises in Fig. 6. The steep curves correspond to isothermal subcooling of the fluid in the bulb, and in the external tubing. Subtracting from dv/dp , the reciprocal of the slope of these curves, the value for the external system (i.e. curves labelled as "correction" in Fig. 6), at the same pressure, yields the compressibility of the liquid at the test temperature and that pressure. The deviation of the compressibility of water by these experiments from that in the Steam Tables (1) is a maximum of 1% from 350°F-500°F, considered a close check due to the relatively small magnitude of liquid phase compressibilities.

b) Saturated Liquid Density

The intersection of the horizontal and the steep portions of the curves in Fig. 6 corresponds to exact filling of the capsule bulb with saturated liquid. If the mass of liquid in the bulb at this point is known, the saturated density can be calculated. However, a property that is more readily obtained is the change in density of saturated liquid from one temperature to another. This is done by raising (or lowering) the temperature of the capsule and measuring the volume of liquid that needs to be removed from (or injected into) the capsule to just refill the bulb with saturated liquid. For instance, the intersections of Figs. 6-1 and 6-2 show that a withdrawal of the injector stem of 237.5 degrees arc is required to maintain the capsule bulb filled with saturated liquid water as its temperature rises from 464.73°F to 473.51°F. After applying the significant corrections for thermal expansion and compressibility, the above result corresponds to a change in density of saturated water, between these temperatures, of 0.4348 lbs/ft. This may be compared with 0.4337 lbs/ft. from the Steam Tables.(5)

It is also possible to determine density of the saturated vapor, and of the change from saturated vapor to saturated liquid, based on an initial state of empty capsule, or capsule filled with saturated vapor at a desired temperature.

c) Vapor Pressure

The saturated vapor pressure is also easily obtained by this method. At any temperature, the horizontal portion of the pressure vs. displacement curve gives the vapor pressure, e.g. in Fig. 6-4a, vapor pressure is 602 psia at 486°F, compared to a steam Table value of 595 psia. Accuracy of vapor pressure suffers from the large volume, and uncertainty of the maximum temperature.

Figs. 7 and 8 show in a comprehensive way the reliability of the experimental values for the vapor pressure and P - ρ - T data from a water test. The overall error of these results is generally less than 1% (3σ).

5. Bibliography

5. J.H. Keenan, F.J. Keyes, T.G. Hill and J.G. Moore, "Steam Tables", Wiley and Sons, Inc. (1969).

D. Thermal Conductivity of Mercury Vapor

During the 1974-1975 contract year the final experiments in the general program of determining thermal conductivity of mercury vapor at higher temperatures than heretofore were carried out and analyzed to determine the corresponding thermal conductivity values. The experimental technique employed alternating current in a fine hot wire, as developed over recent years in this laboratory.

The practical purposes of this program were to provide data to facilitate the design of possible improved topping cycles for fossil fuel power plants, and for nuclear-powered cycles for deep space probes, using mercury as the power cycle working fluid. Added fundamental objectives were to interpret phenomena observed in the condensation of alkali metal vapors, which also polymerize in the vapor state, but with which tests are more difficult, and also to further study the liquid metal state up to the critical region. This fundamental objective has, however, been curtailed as regards mercury, in view of the current increasing need for reliable high temperature information on sodium and lithium. The final result of this program is intended to be a review and handbook of the new, and selected best other, thermophysical properties of mercury. This material is now in the hands of a collaborator, Dr. David Miller, who has been analyzing the literature.

The final data extend thermal conductivity measurements from an earlier study of the saturated and superheated vapor (5) up to a maximum of 920°C and 215 atmospheres abs., or 1690°F and 3160 lbs/sq.in.abs. The four groups of points measured in

FIG - 8

EXPERIMENTAL P-P-T CURVES
FOR WATER

the completed high pressure thermal conductivity program cover the following ranges:

<u>Liquid Temperature</u> (°C)	<u>(Saturation) Pressure</u> (Atm.abs.)	<u>Vapor Superheat</u> (°C)	<u>Thermal Conductivity</u> (BTU/hr.ft.F)
275-284	0.183-0.228	2.-41.	0.00409-0.00437
440-453	3.8-4.5	5.-41.	0.00677-0.00690
695-701	52.-55.	2.5-75.	0.00959-0.0102
915-920	209.-215.	7.-80.	0.0120-0.0128

These results are in the process of being correlated by the use of information available on the dimerization of mercury vapor (7). A preliminary plot (Fig. 9) compares the earlier (6) and present data. It is seen that there is fairly good agreement on the effect of superheat (the spacing of the curves) and on the effect of temperature (the slope of the curves at their "junction"). However, there is a step mismatch in thermal conductivity of about 7% lower for the new high pressure thermal conductivity values, corresponding to good agreement about 20°C lower, compared to the earlier low pressure data. This will be further investigated when analysis of the new high pressure data is completed.

(6) H.S. Erginoz and C.F. Bonilla, "Thermal Conductivity of Mercury Vapor". Proc. of the Fifth Symposium on Thermophysical Properties, pp 64-71, Amer.Soc.Mech.Engrs. (Boston, 1970).

(7) J.A. Siegel, Dr. of Eng'g Sci. dissertation in Nuclear Engineering, with C.F. Bonilla (1975-76).

E. Sodium Loop

Formal offer, and preparation for shipment, of the Control Rod Test Loop, at the General Electric Co. in Evendale, Ohio, were finally completed last winter, and it was brought to Columbia. Substantial repairs were necessary to the electrical power and control circuits, but these have now been completed and the loop installed and connected to power. At present the loop is about to be emptied and cleaned of its NaK. Then the test section with a cavitator and sonic detection transducer will be installed and the loop charged with sodium. The first objective is to provide incipient cavitation information for standard cavitation devices (a Venturi and a nozzle) with sodium and with water (the water tests are already completed). Then a design procedure will be developed whereby incipient and desinent cavitation tests with water on full-sized LMFBR components can be interpreted to accurately predict when cavitation will initiate, and how it can be stopped, under LMFBR operating conditions, so as to design its avoidance, or elimination if it appears. This loop is being installed at Columbia at no cost to E(11-1)-3027, and will be available for any appropriate tests or research of value to the LMFBR program, etc. Figure 10 is a diagram of the loop.

C. F. Bonilla

FIGURE 10. CONTROL ROD LOOP SCHEMATIC