it is not surprising that they respond similarly toward salt solutions. It appears that secondary amines may be slightly superior to the tertiary amines.

Table II and Figure 5 show the results of a study which confirms the validity of the expression $K = (K_+ K_-)^{1/2}$. Gradient quantities of adipic and oleic acid were added to diisopropylamine and equilibrated with 0.1% salt solution. These acids add foreign ions to the system and increase considerably the supply of amine ions.

The adipic acid, being water-soluble, increases the supply of anions in the water phase, raising the sodium selectivity. The water content of the amine phase is reduced, probably through increase in the electrolyte content of the water phase. Oleic acid suppresses the sodium selectivity. The water content of the amine is increased, probably through solvation with the oleate ions. Although the individual ionic selectivities were affected radically, the mean selectivity was unaffected, except by the variation in water content. The results obtained with these acids agree with the other secondary amine data.

## ACKNOWLEDGMENT

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# High Temperature *PVT* Properties of Sodium, Potassium, and Cesium

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**Pressure-volume-temperature properties are presented for three alkali metals—sodium, potassium, and cesium. The data for each metal cover an extended temperature range from the normal boiling point to 2550° F.**

ALKALI METALS, because of their high latent heats of vaporization and heat-transfer coefficients, are prominent candidates for working fluids in turbine power converters. The selection of a particular metal will be largely determined by the maximum cycle temperature, which is limited and effectively fixed by the state of the art for turbine, reactor, and containment materials. Potassium and cesium have vapor pressure ranges which make them attractive for the current state of the art. However, as technology progresses, higher boiling metals such as sodium and lithium will be considered. To evaluate the performance of these alkali metals, a reliable body of experimentally determined physical and thermodynamic properties at proposed operating conditions is required. A program was established to determine several physical and thermodynamic properties of sodium to 2500° F., potassium to 2300° F., and cesium to 2300° F.

This article, which describes pressure-volume-temperature measurements for sodium, potassium, and cesium, is the first publication derived from this program. An ultimate objective is the derivation of reliable engineering and thermodynamic properties—enthalpy, entropy, specific heat, and specific volume. The *PVT* data reported in this article, combined with measurements now in progress of saturation pressures, liquid specific volumes, and liquid specific heats, will provide the experimental data required to obtain these properties.

## EXPERIMENTAL

**Apparatus and Method.** A *PVT* determination requires the measurement of four variables—weight, volume, temperature, and pressure of the vapor involved. For the alkali metals all four of these had to be obtained with high accuracy in order to permit the generation of reliable thermodynamic properties. This was accomplished with a simple constant-volume apparatus using a thin metal diaphragm operating at temperature. The important variable, pressure, was read with sensors at room temperature by balancing the external gas pressure against that of the metal vapor. Temperatures were observed with thermocouples; the alkali metal charge was determined by weighing, and the volume by dimensioning. The method thus permitted the use of direct and positive techniques for obtaining the four basic measurements. The principal disadvantage was that a new or a completely reworked apparatus was required for each experiment, but even this increased the over-all accuracy by reducing systematic errors.

The apparatus, shown in Figure 1, was a small pot equipped with the pressure-sensing diaphragm and a small tube for filling, evacuating, and closing. The principle of the diaphragm design was taken from White and Hilsenrath (*5*). Although it was necessary to redesign their apparatus completely to permit high-temperature operation, the three basic criteria which they suggested for an apparatus of this type were met. The modified apparatus had high sensitivity over the entire temperature and pressure range, a reproducible null point, and a negligible change in volume upon actuation of the diaphragm.

To meet the experimental conditions imposed by temperature and containment, the entire apparatus except for the mullite insulator was fabricated from a refractory alloy, columbium-1% zirconium. This alloy, with a melting point of 4375° F. and a yield strength of around 6000 p.s.i. at 2500° F., proved to be an excellent choice. The mechanical properties of electron beam-melted material were particularly well suited to this work. The sensitivities of diaphragms made from the material were shown experimentally to remain unchanged after repeated cycling from room temperature to 2550° F. Dimensional changes of apparatus after firing were surprisingly low and generally within the expected error of the dimensioning technique. The ma-

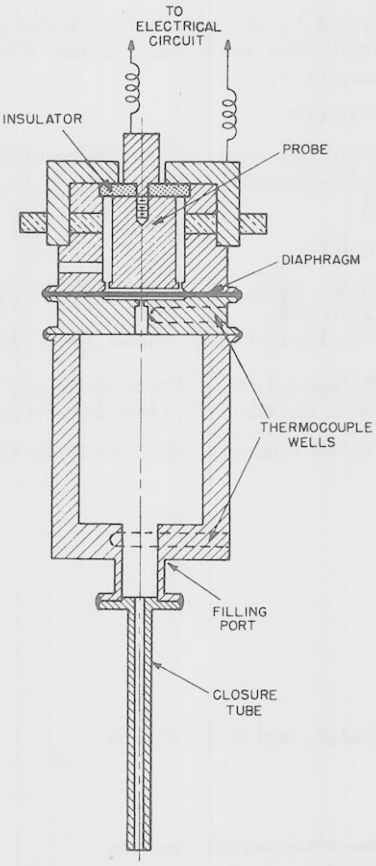

Figure 1. Apparatus

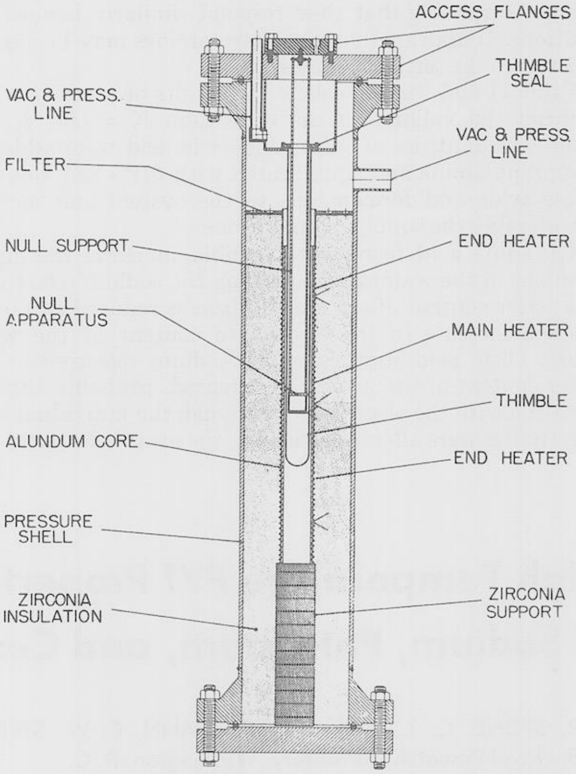

Figure 2. High pressure furnace

chining and welding characteristics were also excellent and helium-tight containers were consistently fabricated.

The deleterious effect of oxygen and nitrogen on the mechanical properties of the refractory alloy required positive protection for each apparatus. To provide both protection and a means for external pressurization for diaphragm operation, and electric furnace was built within a pressure shell. As shown in Figure 2, an Alundum core heater with three molybdenum windings was mounted at the center of the shell and insulated from it with zirconia bubble.

In order to avoid a positive degassing of the high surface area of the insulation particles, the furnace interior was divided into two chambers; an inner chamber, in which the apparatus was located, was separated from the heater windings and insulation by a closed-end mullite tube or thimble. Auxiliary piping and control systems permitted the two chambers to be evacuated and pressurized independently. Purified argon (oxygen content < 1 p.p.m.) was supplied to both chambers by passing welding-grade gas through pressurized trains of molecular sieve and hot titanium sponge.

The procedure for a typical *PVT* experiment was as follows. A Cb–1%Zr capsule of predetermined volume was filled with vacuum-distilled alkali metal and placed in an apparatus through the filling port (Figure 1). The closure tube was welded on, the apparatus evacuated and heated, and the tube welded off. Then, the loaded apparatus with thermocouples installed above and below the chamber, was supported inside the thimble of the pressure furnace (Figure 2) and equlilbrium measurements of temperature and pressure were made over the required range. The furnace pressure was adjusted at each measurement temperature so that the diaphragm was alternately making and breaking electrical contact with the probe. Under these conditions, the furnace pressure (except for a small deflection correction) was equal to the pressure of the metal vapor, and this pressure was observed externally at room temperature with calibrated Bourdon-tube gages.

**Purity of Alkali Metals.** *PVT* results are sensitive to small amounts of impurities and special techniques were required to transfer and purify metal samples. Samples of sodium, potassium, and cesium of the highest available purity were obtained. These, in turn, were introduced into small retorts and distilled into test tube–like ampoules of the columbium alloy for subsequent transfer into the apparatus. Typical analyses of metal samples are presented in another publication (*1*). The metalic impurities reported may be present in either elemental or bound form, but the concentrations in each metal are so low that the maximum error reflected in any *PVT* result is within the precision of the measurement. Although some oxide is probably present in the original charge of each metal, it should have negligible effect on the *PVT* results, since it is gettered at operating temperatures by the refractory metals of the container.

**Diaphragm Operation.** The crucial part of the null-point apparatus is the thin metal diaphragm (0.005 inch thick and 1.6 inches in free diameter) which must operate reproducibly at temperatures to 2550° F. To ensure this reproducibility of motion, diaphragms (made from flat, annealed sheet) which reacted evenly and smoothly to pressure differentials were selected, and each apparatus was machined with fine tolerances so that the position of the probe relative to the diaphragm could be established and maintained constant throughout a series of measurements. This position was adjusted initially in each apparatus so that the probe was within 0.0005 inch of the equilibrium position of the diaphragm. Under these conditions, a finite pressure differential was required to make electrical contact between the diaphragm and the probe. Although this difference was usually below 0.1 p.s.i., it was a significant correction which had to be applied to the observed pressures. The magnitude of the correction for each apparatus was determined experimentally at room temperature before and after each *PVT* experiment. Although these generally agreed within ±0.02 p.s.i., the initial correction was always used, since the probe assembly necessarily received considerable handling after an experiment.

Table I. *PVT* Properties of Sodium

| Temp., °F. | Press., P.S.I.A. | Spec. Vol., Cu. Ft./Lb. |
|---|---|---|
| Experiment 3 | | |
| 2126.7 | 97.33 | 10.750 |
| 2231.4 | 103.36 | 10.767 |
| 2324.3 | 108.38 | 10.783 |
| 2414.3 | 113.17 | 10.798 |
| 2508.6 | 117.94 | 10.814 |
| 2472.8 | 116.23 | 10.808 |
| 2376.9 | 111.22 | 10.792 |
| 2287.8 | 106.34 | 10.777 |
| 2185.9 | 100.82 | 10.760 |
| 2113.3 | 96.68 | 10.748 |
| 2095.5 | 95.20 | 10.745 |
| 2099.3 | 95.48 | 10.746 |
| 2102.9 | 95.73 | 10.746 |
| Experiment 4 | | |
| 1807.3 | 28.27 | 33.399 |
| 1959.8 | 31.10 | 33.472 |
| 2110.5 | 33.80 | 33.547 |
| 2333.5 | 37.39 | 33.662 |
| 2445.5 | 39.11 | 33.722 |
| 2537.2 | 40.49 | 33.772 |
| 2397.9 | 38.34 | 33.697 |
| 2258.1 | 36.16 | 33.623 |
| 2157.4 | 34.55 | 33.571 |
| 2059.3 | 32.91 | 33.522 |
| 2019.4 | 32.23 | 33.502 |
| 1891.2 | 30.02 | 33.439 |
| 1825.2 | 28.81 | 33.407 |
| 1767.4 | 27.70 | 33.380 |
| 1758.2 | 27.38 | 33.375 |
| Experiment 7 | | |
| 2571.6 | 365.00 | 3.0693 |
| 2572.3 | 365.20 | 3.0693 |
| 2576.5 | 366.45 | 3.0695 |
| 2579.0 | 367.15 | 3.0696 |
| 2581.9 | 368.05 | 3.0698 |
| 2582.6 | 368.20 | 3.0698 |
| 2586.4 | 369.20 | 3.0700 |
| 2588.0 | 369.55 | 3.0701 |
| 2579.9 | 367.60 | 3.0697 |
| Experiment 17 | | |
| 2534.3 | 308.95 | 3.6747 |
| 2416.1 | 306.15 | 3.6736 |
| 2506.6 | 304.55 | 3.6730 |
| 2502.7 | 303.85 | 3.6728 |
| 2496.6 | 302.80 | 3.6724 |
| 2495.7 | 302.58 | 3.6724 |
| 2490.5 | 301.36 | 3.6721 |
| Experiment 18 | | |
| 2051.1 | 73.36 | 13.920 |
| 2172.0 | 78.27 | 13.945 |
| 2273.6 | 82.47 | 13.967 |
| 2387.1 | 87.02 | 13.992 |
| 2521.8 | 92.12 | 14.022 |
| 2479.6 | 90.56 | 14.012 |
| Experiment 19 | | |
| 1971.9 | 51.05 | 19.759 |
| 2099.4 | 54.73 | 19.796 |
| 2193.0 | 57.60 | 19.824 |
| 2306.9 | 60.65 | 19.859 |
| 2417.5 | 63.43 | 19.894 |
| 2520.7 | 66.11 | 19.927 |
| 2472.4 | 64.84 | 19.911 |
| 2373.2 | 62.42 | 19.880 |
| 2248.6 | 59.18 | 19.841 |
| 2141.7 | 56.10 | 19.809 |
| 2038.8 | 52.94 | 19.778 |
| 1942.4 | 50.18 | 19.750 |
| 1910.2 | 49.19 | 19.741 |
| Experiment 20 | | |
| 2317.9 | 142.68 | 7.8521 |
| 2382.2 | 147.36 | 7.8600 |
| 2449.4 | 152.37 | 7.8684 |
| 2514.0 | 156.91 | 7.8766 |
| 2486.4 | 155.03 | 7.8731 |
| 2419.5 | 150.13 | 7.8646 |
| 2353.8 | 145.29 | 7.8565 |
| 2284.2 | 140.14 | 7.8479 |
| 2238.1 | 136.73 | 7.8424 |
| 2204.6 | 134.07 | 7.8383 |
| Experiment 23 | | |
| 2399.9 | 194.72 | 5.8001 |
| 2517.3 | 206.52 | 5.8110 |
| 2536.1 | 208.31 | 5.8128 |
| 2491.4 | 204.04 | 5.8086 |
| 2456.3 | 200.27 | 5.8053 |
| 2417.4 | 196.44 | 5.8017 |
| 2373.2 | 192.20 | 5.7977 |
| 2341.9 | 188.99 | 5.7948 |
| 2306.2 | 184.39 | 5.7916 |
| Experiment 25 | | |
| 2439.5 | 253.64 | 4.3766 |
| 2479.2 | 259.12 | 4.3794 |
| 2524.5 | 264.82 | 4.3826 |
| 2511.9 | 263.31 | 4.3817 |
| 2491.8 | 260.78 | 4.3803 |
| 2468.2 | 257.76 | 4.3786 |
| 2452.1 | 255.75 | 4.3775 |
| 2433.5 | 252.91 | 4.3762 |

Table II. *PVT* Properties of Potassium

| Temp., °F. | Press., P.S.I.A. | Spec. Vol., Cu. Ft./Lb. |
|---|---|---|
| Experiment 8 | | |
| 1917.7 | 109.97 | 5.1299 |
| 1960.0 | 112.74 | 5.1331 |
| 2071.9 | 119.83 | 5.1416 |
| 2183.4 | 127.05 | 5.1503 |
| 2282.0 | 132.90 | 5.1581 |
| 2386.8 | 139.26 | 5.1666 |
| 2514.2 | 146.71 | 5.1771 |
| 2476.2 | 144.40 | 5.1739 |
| 2344.1 | 136.85 | 5.1631 |
| 2236.3 | 130.30 | 5.1545 |
| 2118.6 | 123.26 | 5.1452 |
| 2012.4 | 116.46 | 5.1293 |
| 2008.8 | 116.16 | 5.1289 |
| 1920.9 | 110.54 | 5.1302 |
| 1908.9 | 109.64 | 5.1923 |
| 1904.0 | 109.12 | 5.1289 |
| Experiment 9 | | |
| 1830.9 | 77.42 | 7.1196 |
| 1957.1 | 83.70 | 7.1326 |
| 2064.5 | 88.29 | 7.1440 |
| 2171.2 | 92.75 | 7.1555 |
| 2275.0 | 97.27 | 7.1669 |
| 2392.0 | 101.95 | 7.1800 |
| 2515.6 | 107.01 | 7.1942 |
| 2461.3 | 104.82 | 7.1879 |
| 2334.7 | 99.73 | 7.1736 |
| 2223.1 | 94.93 | 7.1611 |
| 2119.7 | 90.58 | 7.1499 |
| 2009.6 | 85.90 | 7.1381 |
| 1881.6 | 79.83 | 7.1248 |
| Experiment 10 | | |
| 2164.5 | 217.72 | 2.7499 |
| 2183.9 | 220.03 | 2.7507 |
| 2286.5 | 232.54 | 2.7550 |
| 2374.9 | 242.88 | 2.7588 |
| 2514.4 | 258.76 | 2.7650 |
| 2439.3 | 250.10 | 2.7616 |
| 2340.7 | 238.65 | 2.7573 |
| 2227.1 | 225.25 | 2.7525 |
| 2148.1 | 215.85 | 2.7492 |
| Experiment 11 | | |
| 2315.8 | 323.62 | 1.8875 |
| 2383.0 | 335.73 | 1.8895 |
| 2512.4 | 357.75 | 1.8934 |
| 2460.9 | 349.01 | 1.8918 |
| 2420.2 | 342.17 | 1.8906 |
| 2351.5 | 330.30 | 1.8885 |
| Experiment 12 | | |
| 2134.0 | 163.91 | 3.7301 |
| 2290.3 | 177.24 | 3.7391 |
| 2365.7 | 183.33 | 3.7435 |
| 2522.8 | 196.11 | 3.7529 |
| 2517.4 | 195.69 | 3.7525 |
| 2485.0 | 193.17 | 3.7506 |
| 2431.6 | 188.96 | 3.7474 |
| 2351.5 | 182.19 | 3.7426 |
| 2258.6 | 174.58 | 3.7372 |
| 2200.1 | 169.61 | 3.7339 |
| 2087.8 | 159.78 | 3.7275 |
| 2046.4 | 156.26 | 3.7252 |
| Experiment 14 | | |
| 2215.1 | 256.18 | 2.3471 |
| 2309.9 | 269.75 | 2.3505 |
| 2426.0 | 285.75 | 2.3548 |
| 2524.7 | 299.10 | 2.3586 |
| 2463.9 | 291.04 | 2.3562 |
| 2409.6 | 283.69 | 2.3542 |
| 2359.3 | 276.61 | 2.3523 |
| 2286.9 | 266.52 | 2.3497 |
| 2242.8 | 260.56 | 2.3481 |
| 2234.1 | 259.35 | 2.3478 |
| 2226.3 | 258.29 | 2.3475 |
| 2204.6 | 254.88 | 2.3467 |
| Experiment 15 | | |
| 1646.8 | 35.23 | 14.903 |
| 1753.3 | 37.63 | 14.926 |
| 1863.8 | 39.97 | 14.949 |
| 1939.5 | 41.56 | 14.965 |
| 2070.6 | 44.20 | 14.994 |
| 2184.4 | 46.40 | 15.020 |
| 2291.3 | 48.49 | 15.045 |
| 2413.7 | 50.80 | 15.074 |
| 2500.3 | 52.30 | 15.095 |
| 2523.8 | 52.75 | 15.101 |
| 2466.0 | 51.72 | 15.087 |
| 2367.3 | 49.94 | 15.063 |
| 2233.3 | 47.42 | 15.032 |
| 2133.5 | 45.50 | 15.009 |
| 2010.6 | 43.01 | 14.981 |
| 1821.3 | 39.15 | 14.940 |
| 1721.6 | 37.01 | 14.919 |
| 1609.7 | 34.52 | 14.896 |
| Experiment 21 | | |
| 1968.3 | 129.27 | 4.4235 |
| 2087.2 | 138.13 | 4.4313 |
| 2197.0 | 145.95 | 4.4387 |
| 2314.7 | 154.36 | 4.4467 |
| 2405.0 | 160.40 | 4.4531 |
| 2519.7 | 168.31 | 4.4612 |
| 2472.0 | 165.11 | 4.4578 |
| 2366.1 | 157.74 | 4.4503 |
| 2260.3 | 150.49 | 4.4430 |
| 2149.9 | 142.54 | 4.4355 |
| 2055.4 | 135.78 | 4.4292 |
| 1978.6 | 130.10 | 4.4241 |
| Experiment 22 | | |
| 2443.5 | 400.75 | 1.5880 |
| 2453.9 | 402.95 | 1.5882 |
| 2449.4 | 401.95 | 1.5881 |
| 2428.7 | 397.85 | 1.5876 |
| 2431.8 | 398.40 | 1.5877 |
| 2416.5 | 395.41 | 1.5873 |
| 2413.9 | 394.71 | 1.5872 |
| 2409.1 | 393.35 | 1.5871 |
| 2406.9 | 392.90 | 1.5870 |

In addition, the deflection correction is temperature-dependent. To determine the influence of temperature, a series of experiments was made using a blank apparatus in which the probe was spaced to give a correction several times that normally observed. The pressure required to make (or break) electrical contact between this probe and its diaphragm was measured from room temperature to 2500° F. The room temperature value of each working apparatus was assumed to have the same temperature dependency as that exhibited by the blank apparatus, and was adjusted accordingly.

## RESULTS

Superheat properties of the three alkali metals are presented in Tables I, II, and III. Those for potassium are also presented graphically in Figure 3, where observed pressures and temperatures are plotted for the individual experiments.

The results shown in Figure 3 for potassium are typical of those for the other metals. The several experiments for each metal cover a wide range in the superheat region with temperatures extending from just above the normal boiling point to at least 2500° F. and pressures extending from 1 or 2 atm. to 21 atm. for sodium, 27 atm. for potassium, and 33 atm. for cesium. Equilibrium measurements for each experiment were generally made over at least one full temperature cycle. The final pressure and temperature for each state were obtained by taking readings at 5- to 10-minute intervals until successive temperatures showed a drift of less than 0.08° F. per minute and a difference across the apparatus of less than 2° F. The specific volume at each state was computed using the weight of metal added and the volume

Table III. *PVT* Properties of Cesium

| Temp., °F. | Press., P.S.I.A. | Spec. Vol., Cu. Ft./Lb. |
|---|---|---|
| Experiment 27 | | |
| 1785.3 | 102.71 | 1.5321 |
| 1953.8 | 113.12 | 1.5358 |
| 2095.4 | 121.32 | 1.5390 |
| 2201.6 | 127.55 | 1.5415 |
| 2319.7 | 134.06 | 1.5443 |
| 2425.8 | 140.03 | 1.5469 |
| 2558.6 | 147.11 | 1.5502 |
| 2520.4 | 145.09 | 1.5492 |
| 2366.6 | 136.82 | 1.5454 |
| 2262.5 | 131.00 | 1.5429 |
| 2163.2 | 125.54 | 1.5406 |
| 2044.8 | 118.30 | 1.5378 |
| 1884.5 | 108.95 | 1.5342 |
| 1826.2 | 105.32 | 1.5329 |
| 1724.3 | 99.00 | 1.5307 |
| 1741.1 | 100.06 | 1.5311 |
| Experiment 28 | | |
| 1649.0 | 71.26 | 2.0879 |
| 1703.2 | 73.84 | 2.0894 |
| 1822.0 | 79.04 | 2.0929 |
| 1612.7 | 69.73 | 2.0868 |
| 1737.2 | 75.51 | 2.0904 |
| 1854.8 | 80.54 | 2.0939 |
| 1978.8 | 86.15 | 2.0977 |
| 2081.0 | 90.31 | 2.1009 |
| 2178.4 | 94.33 | 2.1040 |
| 2275.0 | 98.41 | 2.1071 |
| 2379.1 | 102.45 | 2.1105 |
| 2485.2 | 106.67 | 2.1141 |
| 2565.6 | 110.04 | 2.1169 |
| 2523.2 | 108.31 | 2.1154 |
| 2441.6 | 104.98 | 2.1126 |
| 2329.0 | 100.63 | 2.1089 |
| 2221.4 | 96.29 | 2.1054 |
| 2116.9 | 91.88 | 2.1020 |
| 2038.2 | 88.66 | 2.0995 |
| 1919.5 | 83.75 | 2.0959 |
| 1766.5 | 76.76 | 2.0913 |
| 1624.3 | 70.43 | 2.0871 |
| 1647.5 | 71.41 | 2.0878 |
| Experiment 30 | | |
| 1341.5 | 16.88 | 8.0140 |
| 1460.8 | 18.28 | 8.0266 |
| 1581.4 | 19.67 | 8.0397 |
| 1712.7 | 21.07 | 8.0543 |
| 1777.9 | 21.71 | 8.0617 |
| 1901.5 | 22.95 | 8.0760 |
| 1996.8 | 23.92 | 8.0873 |
| 2094.8 | 24.92 | 8.0991 |
| 2212.0 | 26.09 | 8.1135 |
| 2314.1 | 27.08 | 8.1263 |
| 2424.6 | 28.15 | 8.1405 |
| 2571.4 | 29.59 | 8.1597 |
| 2518.7 | 29.08 | 8.1528 |
| 2465.0 | 28.54 | 8.1457 |
| 2369.2 | 27.67 | 8.1333 |
| 2257.5 | 26.55 | 8.1192 |
| 2139.4 | 25.41 | 8.1045 |
| 2029.2 | 24.29 | 8.0912 |
| 1948.5 | 23.47 | 8.0815 |
| 1847.8 | 22.43 | 8.0697 |
| 1649.8 | 20.36 | 8.0473 |
| 1515.0 | 18.89 | 8.0325 |
| 1391.1 | 17.49 | 8.0192 |
| 1305.0 | 16.50 | 8.0103 |
| Experiment 31 | | |
| 1909.1 | 141.31 | 1.1606 |
| 2037.4 | 151.77 | 1.1628 |
| 2143.7 | 159.91 | 1.1646 |
| 2236.7 | 167.16 | 1.1663 |
| 2363.0 | 176.84 | 1.1686 |
| 2462.0 | 183.92 | 1.1704 |
| 2568.2 | 191.70 | 1.1724 |
| 2518.6 | 188.11 | 1.1715 |
| 2415.6 | 180.62 | 1.1695 |
| 2305.0 | 172.26 | 1.1675 |
| 2186.5 | 163.35 | 1.1654 |
| 2081.2 | 155.17 | 1.1635 |
| 1959.5 | 145.34 | 1.1614 |
| 1827.0 | 134.59 | 1.1592 |
| Experiment 32 | | |
| 1846.9 | 137.66 | 1.1468 |
| 1944.1 | 145.62 | 1.1484 |
| 2058.5 | 155.03 | 1.1504 |
| 2175.7 | 164.24 | 1.1524 |
| 2291.4 | 173.14 | 1.1545 |
| 2396.2 | 181.22 | 1.1564 |
| 2497.5 | 189.09 | 1.1582 |
| 2558.8 | 193.53 | 1.1594 |
| 2452.0 | 185.36 | 1.1574 |
| 2363.8 | 179.03 | 1.1558 |
| 2238.3 | 169.34 | 1.1535 |
| 2140.1 | 161.55 | 1.1518 |
| 1973.9 | 148.17 | 1.1489 |
| 1894.9 | 141.71 | 1.1476 |
| 1830.5 | 136.42 | 1.1465 |
| Experiment 34 | | |
| 2068.0 | 223.98 | 0.75273 |
| 2174.2 | 237.42 | 0.75394 |
| 2184.2 | 238.73 | 0.75405 |
| 2294.0 | 252.35 | 0.75533 |
| 2387.8 | 263.62 | 0.75644 |
| 2483.7 | 275.15 | 0.75760 |
| 2543.1 | 282.34 | 0.75833 |
| 2516.5 | 279.07 | 0.75800 |
| 2437.0 | 269.82 | 0.75703 |
| 2347.6 | 258.97 | 0.75596 |
| 2247.9 | 246.84 | 0.75479 |
| 2119.4 | 230.73 | 0.75331 |
| 2024.9 | 218.68 | 0.75225 |
| Experiment 35 | | |
| 2126.4 | 259.51 | 0.65739 |
| 2223.6 | 273.52 | 0.65836 |
| 2329.0 | 288.58 | 0.65944 |
| 2492.0 | 211.00 | 0.66115 |
| 2447.0 | 304.60 | 0.66067 |
| 2401.2 | 298.43 | 0.66019 |
| 2290.3 | 283.09 | 0.65904 |
| 2172.1 | 266.03 | 0.65784 |
| 2061.6 | 250.03 | 0.65675 |
| Experiment 36 | | |
| 2300.6 | 383.74 | 0.45493 |
| 2397.6 | 404.19 | 0.45563 |
| Experiment 37 | | |
| 2405.0 | 460.27 | 0.38763 |
| 2512.7 | 486.61 | 0.38830 |
| 2519.7 | 488.25 | 0.38835 |
| 2487.5 | 480.38 | 0.38815 |
| 2445.9 | 470.10 | 0.38789 |
| 2355.1 | 447.79 | 0.38733 |
| 2315.1 | 437.63 | 0.38709 |
| Experiment 38 | | |
| 1578.9 | 49.49 | 3.0146 |
| 1684.9 | 52.31 | 3.0190 |
| 1801.0 | 55.91 | 3.0239 |
| 1921.5 | 59.76 | 3.0292 |
| 2015.7 | 62.26 | 3.0334 |
| 2136.8 | 65.57 | 3.0389 |
| 2230.5 | 68.32 | 3.0432 |
| 2348.2 | 71.58 | 3.0488 |
| 2437.7 | 74.08 | 3.0531 |
| 2523.8 | 76.28 | 3.0574 |
| 2479.4 | 75.18 | 3.0552 |
| 2314.0 | 70.78 | 3.0472 |
| 2193.8 | 67.29 | 3.0415 |
| 2076.7 | 64.07 | 3.0361 |
| 1970.3 | 61.16 | 3.0314 |
| 1864.1 | 58.16 | 3.0267 |
| 1777.8 | 55.37 | 3.0230 |
| 1640.8 | 51.26 | 3.0172 |
| 1521.8 | 47.49 | 3.0123 |
| Experiment 39 | | |
| 2183.7 | 319.75 | 0.52803 |
| 2320.2 | 344.44 | 0.52915 |
| 2423.6 | 362.86 | 0.53001 |
| 2540.7 | 383.04 | 0.53101 |
| 2487.0 | 373.87 | 0.53055 |
| 2379.4 | 355.24 | 0.52964 |
| 2260.0 | 333.85 | 0.52865 |
| 2222.7 | 327.09 | 0.52835 |
| 2149.9 | 313.85 | 0.52776 |
| Experiment 40 | | |
| 2355.6 | 401.33 | 0.44574 |
| 2469.1 | 425.81 | 0.44654 |
| 2527.9 | 438.24 | 0.44696 |
| 2414.6 | 414.63 | 0.44615 |
| 2309.9 | 392.31 | 0.44542 |
| 2263.9 | 382.06 | 0.44510 |
| 2228.8 | 374.62 | 0.44486 |

of the chamber. This volume was nominally 57 or 113 cc., with the larger apparatus being used for only four experiments (9 and 15 for potassium, 18 and 19 for sodium). The predetermined weight of the metal charge for a given experiment was dictated by the volume of the apparatus and the desired pressure range; the charges of sodium varied from 0.0281 to 0.3076 gram, potassium from 0.1240 to 0.5892 gram, and cesium from 0.1173 to 2.4205 gram.

Specific volumes of several saturated vapor states for each metal (Table IV) were directly observed. The measurements were made in the course of the *PVT* studies, and each value represents an intersection of the saturated and superheated vapor curves for one of the experiments. However, observed pressures near the intersection points were invariably low. Figure 4 illustrates this phenomenon for a typical experiment. For a short temperature range, observed pressures are below the true saturation and superheat curves. The depressed curve in this region was reproducible and was independent of both the magnitude and direction of the temperature difference across the chamber. 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 values. For this reason, the saturated specific volumes were obtained by short extrapolations of the superheated vapor curves to the true saturation curve as defined by the vapor-pressure equation (*1*).

Compressibility factor–pressure isotherms covering the experimental range of each metal are presented in Figure 5. Factors for the superheated vapors at the selected temperatures were computed from smoothed data obtained from large-scale plots of the experimental pressures and temperatures in Tables I, II, and III. Factors for the saturated vapors were computed from the data in Table IV. These diagrams may be used to obtain specific volume information for the saturated and superheated vapors. In addition, they illustrate the precision of the work and the thermodynamic similarity of the compressibilities for the three metals.

## DISCUSSION

It was recognized at the start of this work that a high degree of accuracy in all measurement phases would be required if reliable thermodynamic quantities were to be derived. Therefore, the design of both apparatus and method was approached from the standpoint of obtaining maximum accuracy. The steps taken in this direction are discussed in the following paragraphs.

Pressures were observed with three precision Wallace and Tiernan gages with ranges of 0 to 50, 0 to 300, and 0 to 500 p.s.i.a. The three gages were calibrated, *in situ*, with deadweight piston gages by personnel of the Eastern Standards Laboratory at intervals of about 6 months. The gages func-

Table IV. Specific Volumes of Saturated Alkali Metal Vapors

| Sodium | | | Potassium | | | Cesium | | |
|---|---|---|---|---|---|---|---|---|
| Expt. No. | Temp., °F. | Spec. vol., cu. ft./lb. | Expt. No. | Temp., °F. | Spec. vol., cu. ft./lb. | Expt. No. | Temp., °F. | Spec. vol., cu. ft./lb. |
| 4 | 1750.1 | 33.37 | 15 | 1570.2 | 14.888 | 30 | 1250.9 | 8.005 |
| 19 | 1888.3 | 19.73 | 9 | 1776.4 | 7.114 | 38 | 1484.3 | 3.011 |
| 18 | 1988.8 | 13.90 | 8 | 1886.9 | 5.127 | 28 | 1588.2 | 2.086 |
| 3 | 2071.8 | 10.74 | 21 | 1939.1 | 4.421 | 27 | 1687.3 | 1.530 |
| 20 | 2177.6 | 7.835 | 12 | 1999.7 | 3.722 | 31 | 1784.8 | 1.159 |
| 23 | 2289.0 | 5.790 | 10 | 2122.2 | 2.748 | 32 | 1789.9 | 1.146 |
| 25 | 2402.3 | 4.374 | 14 | 2191.3 | 2.346 | 34 | 1955.8 | 0.7515 |
| 17 | 2474.4 | 3.671 | 11 | 2289.0 | 1.887 | 35 | 2014.2 | 0.6561 |
| 7 | 2555.1 | 3.069 | 22 | 2376.1 | 1.586 | 39 | 2114.6 | 0.5275 |
| | | | | | | 36 | 2187.0 | 0.4542 |
| | | | | | | 40 | 2197.4 | 0.4448 |
| | | | | | | 37 | 2269.4 | 0.3869 |

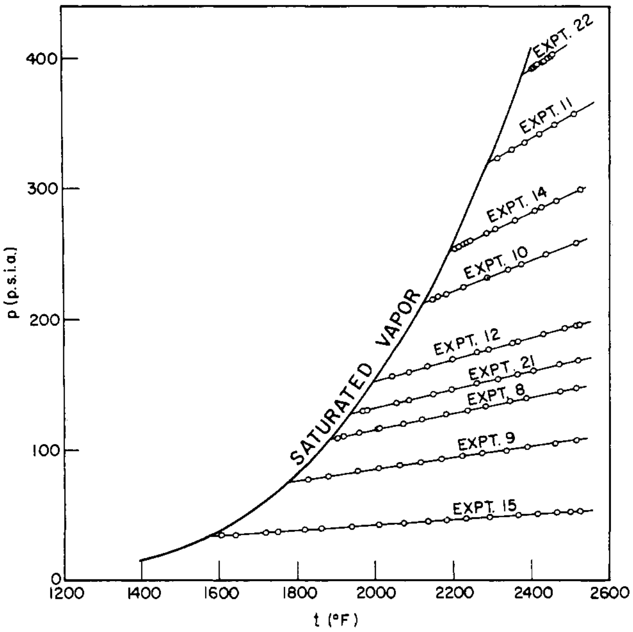

Figure 3. Pressure and temperature observations on superheated potassium vapor

tioned exceptionally well and calibrations were consistently reproduced over a 3-year period.

The weight of metal added to a given chamber was determined by weighing a tared capsule filled with the alkali metal prior to its introduction into the chamber. The semimicrobalance used was checked with calibrated weights prior to and following the weighing of each capsule. It is believed that the observed weights were accurate to within ±0.1 mg. A check of this measurement was obtained indirectly by determination of total alkali at the conclusion of each experiment. Although the precision of this analytical determination was reduced by the number of washings required for complete removal of the alkali metal, the weights by titration analysis allowed an independent check of the observed weights.

The volume of each apparatus was obtained by precise dimensioning of the chamber before and after an experiment. Volumes computed from dimensions taken before and after firing differed randomly by about ±0.1%, and the experimental volume in each case was taken as the arithmetical mean. Corrections for the expansion of the chamber with temperature were accurately computed from expansion data measured at this laboratory. The linear expansion of the columbium alloy as determined with sapphire and quartz dilatometers from 500° to 2550° F. is represented by the following equation,

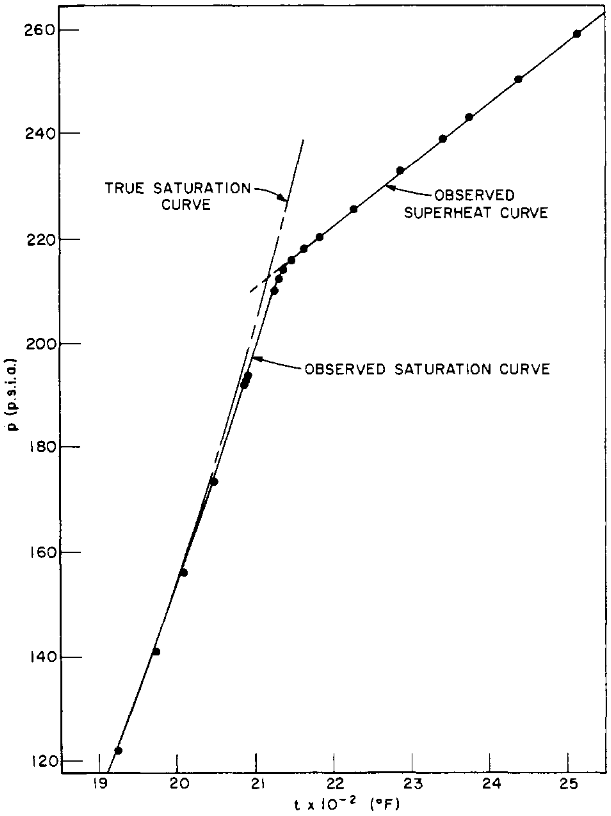

Figure 4. Phenomenon at intersection of saturation and superheat curves

Illustrated with experiment 10

$$L_t = L_o[1.000265 + 3.1854\times10^{-6}\,(t-75) + 4.615\times10^{-10}\,(t-75)^2] \quad (1)$$

where $L_t$ is the length at temperature $t$, °F., and $L_o$ is the length at 75° F.

Temperatures were measured with Pt, 6% Rh-Pt, 30% Rh thermocouples which were calibrated by direct comparison with two types of NBS standardized couples—a Pt, 6% Rh-Pt, 30% Rh calibrated against primary melting points to the gold point and against optical pyrometers from 1800° to 3000° F.; and a Pt-Pt, 10% Rh, likewise calibrated against primary melting points to 1920° F. and extended to 2600° F. with the standard quadratic relationship between e.m.f. and temperature. The measurement thermocouples were also checked for instability by the method outlined by Walker *et al.* (3). Although the observed instabilities were small, it appeared that they might become

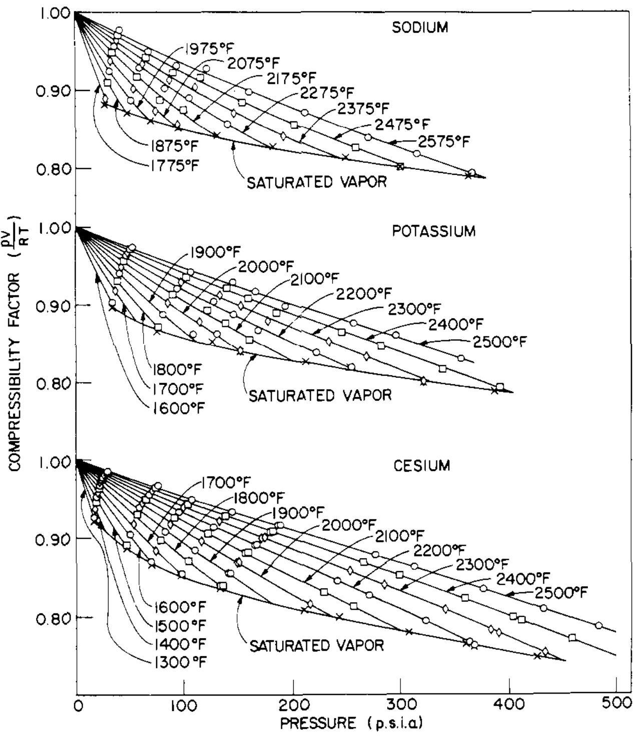

Figure 5. Compressibility factor–pressure diagrams for sodium, potassium, and cesium

significant after three or four cycles to 2500° F. Therefore, thermocouples were used for a maximum of three cycles and then replaced.

At the start of this work, three possible problem areas were recognized: the diffusion of gas through the thin diaphragm at higher temperatures, the inclusion of inert gas in the chambers during the closure operation, and surface adsorption of the alkali metals. The problem of diffusion did not materialize, as evidenced by the reproducibility of pressure readings before and after multiple high-temperature firings. Initially the inclusion of gas in the chamber was a problem, but was eliminated by improved degassing and welding off techniques. Each apparatus was checked for gas at the conclusion of an experiment by opening the chamber to an evacuated manometer with which pressures as low as 0.01 p.s.i. were detectable. Gas was detected in only one of the 30 experiments reported; experiment 12 for potassium contained 0.4 p.s.i. of argon at room temperature. The third problem area, the possibility of significant surface adsorption, was checked experimentally. Two apparatus with significantly different surface-volume ratios were used for both sodium and potassium. The *PVT* properties for each metal as obtained in the two apparatus are internally consistent; this is good evidence that any adsorption of the alkali metal on the container surface was insignificant.

The principal sources which contribute uncertainty to the measured quantities have been discussed, and numerical errors may be assigned. However, it is desirable to express the error in terms of the indirectly measured compressibility factor, since it is often employed directly in the thermodynamic reduction of data. The error in this factor may be calculated from the individual uncertainties by the usual laws for the propagation of error. Probable errors, predicted in this manner, range from ±0.26 to ±0.44% for sodium, ±0.26 to ±0.35% for potassium, and ±0.25 to ±0.28% for cesium (the high values for sodium and potassium occurring in only one or two low-weight experiments). These figures include an estimated uncertainty in the temperature from its value on the thermodynamic scale, and it is expected that they will be larger than the observed precision indices.

Compressibility studies have been performed at lower temperatures for two of the alkali metals. Walling *et al.* (*4*) reported results for potassium in the temperature range from 1560° to 2100° F., and Tepper *et al.* (*2*), results for cesium in the range from 1000° to 2150° F. These may be compared to those generated in the present study. It is impossible to assess and compare systematic errors, but precision indices can and should be compared, since these will predict the relative reliability of the thermodynamic properties which may be generated from the measurements.

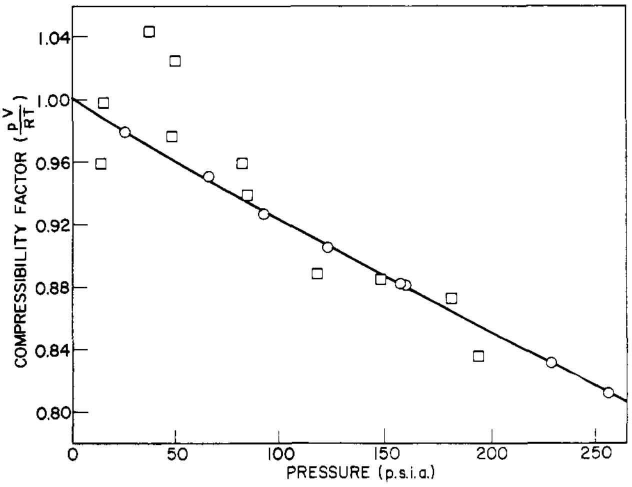

Figure 6. Comparison of observed compressibilities for cesium with those of Tepper at 2096° F.

○ Tepper

☐ This work

Compressibility factors for cesium are compared in Figure 6 at only one temperature near the top of Tepper's experimental range. However, the point spread and precision exhibited by the experimental points at this temperature are typical of those for other isotherms in the overlapping temperature range. This permits one to predict the over-all precision attained in each study from that observed at this one temperature. The average per cent deviations, so estimated, for the cesium measurements of this laboratory and of Tepper *et al.* are ±0.15 and ±1.8%, respectively.

The compressibility factors reported by Walling *et al.* for potassium show random differences of 5 to 10% from those in this article. No further comparison of the data is warranted, since the authors themselves assigned large uncertainties of 5 to 9% to their experimental factors and wisely did not generate thermodynamic properties directly from their compressibility data.

The compressibilities reported in this article are believed to be the most reliable values measured for the alkali metals. They were measured over extended temperature ranges and are of sufficient accuracy to permit the generation of reliable engineering and thermodynamic properties.

## ACKNOWLEDGMENT

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