

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 results obtained with these acid secondary amine data.

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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-

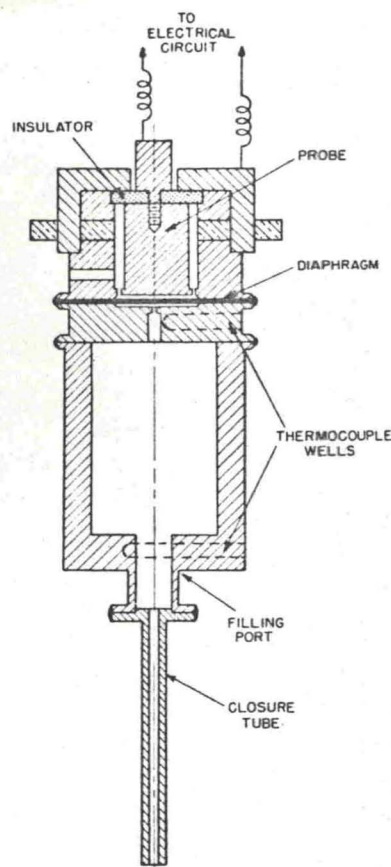


Figure 1. Apparatus

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, an 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 equilibrium 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

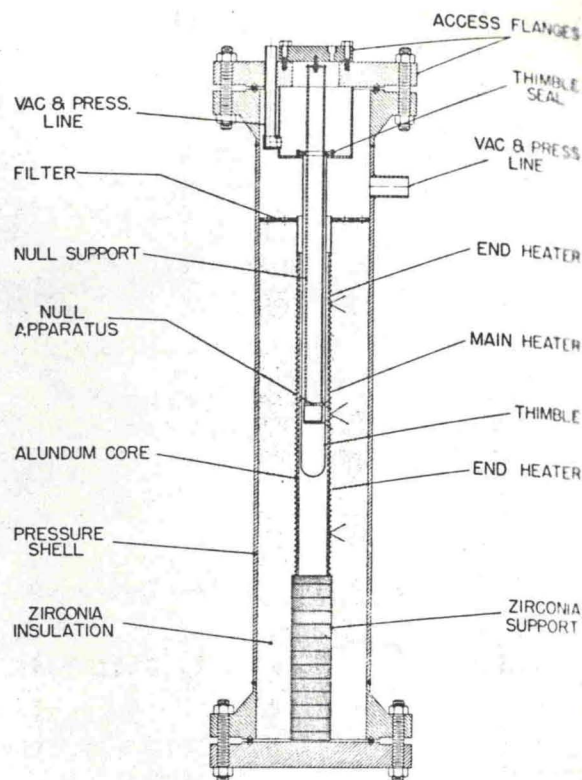


Figure 2. High pressure furnace

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 metallic 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.	Temp., ° F.	Press., P.S.I.A.	Spec. Vol., Cu. Ft./Lb.
Experiment 3			Experiment 18		
205.7	97.33	10.750	2051.1	73.36	13.920
208.4	103.36	10.767	2172.0	78.27	13.945
211.4	108.38	10.783	2273.6	82.47	13.967
214.3	113.17	10.798	2387.1	87.02	13.992
217.6	117.94	10.814	2521.8	92.12	14.022
220.8	116.23	10.808	2479.6	90.56	14.012
223.9	111.22	10.792	Experiment 19		
226.9	106.34	10.777	1971.9	51.05	19.759
229.9	100.82	10.760	2099.4	54.73	19.796
232.8	96.68	10.748	2193.0	57.60	19.824
235.5	95.20	10.745	2306.9	60.65	19.859
238.3	95.48	10.746	2417.5	63.43	19.894
240.9	95.73	10.746	2520.7	66.11	19.927
Experiment 4			2472.4	64.84	19.911
1807.3	28.27	33.399	2373.2	62.42	19.880
1859.8	31.10	33.472	2248.6	59.18	19.841
1910.5	33.80	33.547	2141.7	56.10	19.809
1963.5	37.39	33.662	2038.8	52.94	19.778
2015.5	39.11	33.722	1942.4	50.18	19.750
2067.2	40.49	33.772	1910.2	49.19	19.741
2117.9	38.34	33.697	Experiment 20		
2168.1	36.16	33.623	2317.9	142.68	7.8521
2217.4	34.55	33.571	2382.2	147.36	7.8600
2266.3	32.91	33.522	2449.4	152.37	7.8684
2314.4	32.23	33.502	2514.0	156.91	7.8766
2361.9	30.02	33.439	2486.4	155.03	7.8731
2409.2	28.81	33.407	2419.5	150.13	7.8646
2456.4	27.70	33.380	2353.8	145.29	7.8565
2503.2	27.38	33.375	2284.2	140.14	7.8479
Experiment 7			2238.1	136.73	7.8424
2571.6	365.00	3.0693	2204.6	134.07	7.8383
2572.3	365.20	3.0693	Experiment 23		
2576.5	366.45	3.0695	2399.9	194.72	5.8001
2579.0	367.15	3.0696	2517.3	206.52	5.8110
2581.9	368.05	3.0698	2536.1	208.31	5.8128
2582.6	368.20	3.0698	2491.4	204.04	5.8086
2586.4	369.20	3.0700	2456.3	200.27	5.8053
2588.0	369.55	3.0701	2417.4	196.44	5.8017
2579.9	367.60	3.0697	2373.2	192.20	5.7977
Experiment 17			2341.9	188.99	5.7948
2534.3	308.95	3.6747	2306.2	184.39	5.7916
2416.1	306.15	3.6736	Experiment 25		
2306.6	304.55	3.6730	2439.5	253.64	4.3766
2502.7	303.85	3.6728	2479.2	259.12	4.3794
2496.6	302.80	3.6724	2524.5	264.82	4.3826
2495.7	302.58	3.6724	2511.9	263.31	4.3817
2490.5	301.36	3.6721	2491.8	260.78	4.3803
			2468.2	257.76	4.3786
			2452.1	255.75	4.3775
			2433.5	252.91	4.3762

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.

Table II. PVT Properties of Potassium

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

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.	Temp., ° F.	Press., P.S.I.A.	Spec. Vol., Cu. Ft./Lb.	Temp., ° F.	Press., P.S.I.A.	Spec. Vol., Cu. Ft./Lb.	Temp., ° F.	Press., P.S.I.A.	Spec. Vol., Cu. Ft./Lb.
Experiment 27			Experiment 30			Experiment 32			Experiment 37		
1785.3	102.71	1.5321	1341.5	16.88	8.0140	1846.9	137.66	1.1468	2405.0	460.27	0.38763
1953.8	113.12	1.5358	1460.8	18.28	8.0266	1944.1	145.62	1.1484	2512.7	486.61	0.38833
2095.4	121.32	1.5390	1581.4	19.67	8.0397	2058.5	155.03	1.1504	2519.7	488.25	0.38833
2201.6	127.55	1.5415	1712.7	21.07	8.0543	2175.7	164.24	1.1524	2487.5	480.38	0.38833
2319.7	134.06	1.5443	1777.9	21.71	8.0617	2291.4	173.14	1.1545	2445.9	470.10	0.38789
2425.8	140.03	1.5469	1901.5	22.95	8.0760	2396.2	181.22	1.1564	2355.1	447.79	0.38733
2558.6	147.11	1.5502	1996.8	23.92	8.0873	2497.5	189.09	1.1582	2315.1	437.63	0.38709
2520.4	145.09	1.5492	2094.8	24.92	8.0991	2558.8	193.53	1.1594	Experiment 38		
2366.6	136.82	1.5454	2212.0	26.09	8.1135	2452.0	185.36	1.1574	1578.9	49.49	3.0146
2262.5	131.00	1.5429	2314.1	27.08	8.1263	2363.8	179.03	1.1558	1684.9	52.31	3.0190
2163.2	125.54	1.5406	2424.6	28.15	8.1405	2238.3	169.34	1.1535	1801.0	55.91	3.0239
2044.8	118.30	1.5378	2571.4	29.59	8.1597	2140.1	161.55	1.1518	1921.5	59.76	3.0292
1884.5	108.95	1.5342	2518.7	29.08	8.1528	1973.9	148.17	1.1489	2015.7	62.26	3.0334
1826.2	105.32	1.5329	2465.0	28.54	8.1457	1894.9	141.71	1.1476	2136.8	65.57	3.0389
1724.3	99.00	1.5307	2369.2	27.67	8.1333	1830.5	136.42	1.1465	2230.5	68.32	3.0432
1741.1	100.06	1.5311	2257.5	26.55	8.1192	Experiment 34			2348.2	71.58	3.0488
Experiment 28			2139.4	25.41	8.1045	2068.0	223.98	0.75273	2437.7	74.08	3.0531
1649.0	71.26	2.0879	2029.2	24.29	8.0912	2174.2	237.42	0.75394	2523.8	76.28	3.0574
1703.2	73.84	2.0894	1948.5	23.47	8.0815	2184.2	238.73	0.75405	2479.4	75.18	3.0552
1822.0	79.04	2.0929	1847.8	22.43	8.0697	2294.0	252.35	0.75533	2314.0	70.78	3.0472
1612.7	69.73	2.0868	1649.8	20.36	8.0473	2387.8	263.62	0.75644	2193.8	67.29	3.0415
1737.2	75.51	2.0904	1515.0	18.89	8.0325	2483.7	275.15	0.75760	2076.7	64.07	3.0361
1854.8	80.54	2.0939	1391.1	17.49	8.0192	2483.7	275.15	0.75760	1970.3	61.16	3.0314
1978.8	86.15	2.0977	1305.0	16.50	8.0103	2543.1	282.34	0.75833	1864.1	58.16	3.0267
2081.0	90.31	2.1009	Experiment 31			2516.5	279.07	0.75800	1777.8	55.37	3.0230
2178.4	94.33	2.1040	1909.1	141.31	1.1606	2437.0	269.82	0.75703	1640.8	51.26	3.0172
2275.0	98.41	2.1071	2037.4	151.77	1.1628	2347.6	258.97	0.75596	1521.8	47.49	3.0123
2379.1	102.45	2.1105	2143.7	159.91	1.1646	2247.9	246.84	0.75479	Experiment 39		
2485.2	106.67	2.1141	2236.7	167.16	1.1663	2119.4	230.73	0.75331	2183.7	319.75	0.52803
2565.6	110.04	2.1169	2363.0	176.84	1.1686	2024.9	218.68	0.75225	2320.2	344.44	0.52915
2523.2	108.31	2.1154	2462.0	183.92	1.1704	Experiment 35			2423.6	362.86	0.53001
2441.6	104.98	2.1126	2568.2	191.70	1.1724	2126.4	259.51	0.65739	2540.7	383.04	0.53101
2329.0	100.63	2.1089	2518.6	188.11	1.1715	2223.6	273.52	0.65836	2487.0	373.87	0.53055
2221.4	96.29	2.1054	2415.6	180.62	1.1695	2329.0	288.58	0.65944	2379.4	355.24	0.52964
2116.9	91.88	2.1020	2305.0	172.26	1.1675	2492.0	211.00	0.66115	2260.0	333.85	0.52865
2038.2	88.66	2.0995	2186.5	163.35	1.1654	2447.0	304.60	0.66067	2222.7	327.09	0.52835
1919.5	83.75	2.0959	2081.2	155.17	1.1635	2401.2	298.43	0.66019	2149.9	313.85	0.52776
1766.5	76.76	2.0913	1959.5	145.34	1.1614	2290.3	283.09	0.65904	Experiment 40		
1624.3	70.43	2.0871	1827.0	134.59	1.1592	2172.1	266.03	0.65784	2355.6	401.33	0.44574
1647.5	71.41	2.0878	Experiment 36			2061.6	250.03	0.65675	2469.1	425.81	0.44654
			2300.6	383.74	0.45493	Experiment 33			2527.9	438.24	0.44696
			2397.6	404.19	0.45563	1846.9	137.66	1.1468	2414.6	414.63	0.44615
						1944.1	145.62	1.1484	2309.9	392.31	0.44542
						2058.5	155.03	1.1504	2263.9	382.06	0.44510
						2175.7	164.24	1.1524	2228.8	374.62	0.44486
						2291.4	173.14	1.1545			
						2396.2	181.22	1.1564			
						2497.5	189.09	1.1582			
						2558.8	193.53	1.1594			

Table IV. Specific Volumes of Saturated Alkali Metal Vapors

Spec. Vol. Cu. Ft./Lb. 37	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.
0.38763	4	1750.1	33.37	15	1570.2	14.888	30	1250.9	8.005
0.38830	19	1888.3	19.73	9	1776.4	7.114	38	1484.3	3.011
0.38835	18	1988.8	13.90	8	1886.9	5.127	28	1588.2	2.086
0.38815	3	2071.8	10.74	21	1939.1	4.421	27	1687.3	1.530
0.38789	20	2177.6	7.835	12	1999.7	3.722	31	1784.8	1.159
0.38733	23	2289.0	5.790	10	2122.2	2.748	32	1789.9	1.146
0.38709	25	2402.3	4.374	14	2191.3	2.346	34	1955.8	0.7515
38	17	2474.4	3.671	11	2289.0	1.887	35	2014.2	0.6561
3.0146	7	2555.1	3.069	22	2376.1	1.586	39	2114.6	0.5275
3.0190							36	2187.0	0.4542
3.0239							40	2197.4	0.4448
3.0292							37	2269.4	0.3869
3.0334									
3.0389									
3.0432									
3.0488									
3.0531									
3.0574									
3.0552									
3.0472									
3.0415									
3.0361									
3.0314									
3.0267									
3.0230									
3.0172									
3.0123									
39									
0.52803									
0.52915									
0.53001									
0.53101									
0.53055									
0.52964									
0.52865									
0.52835									
0.52776									
40									
0.44574									
0.44654									
0.44696									
0.44615									
0.44542									
0.44510									
0.44486									

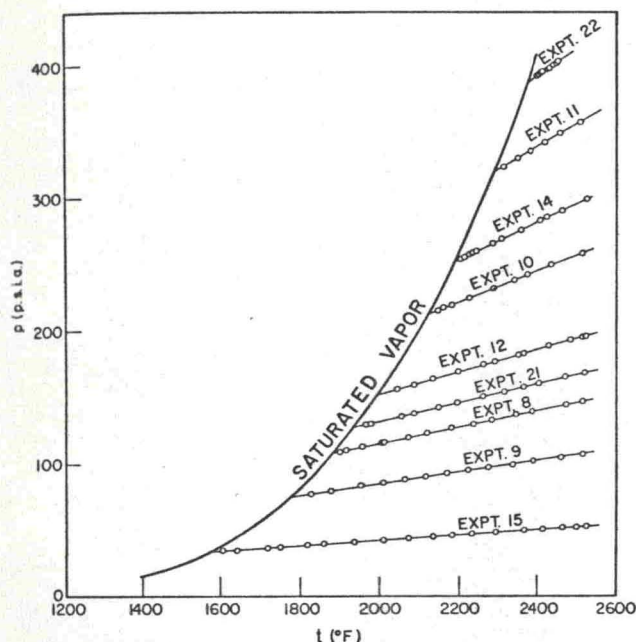
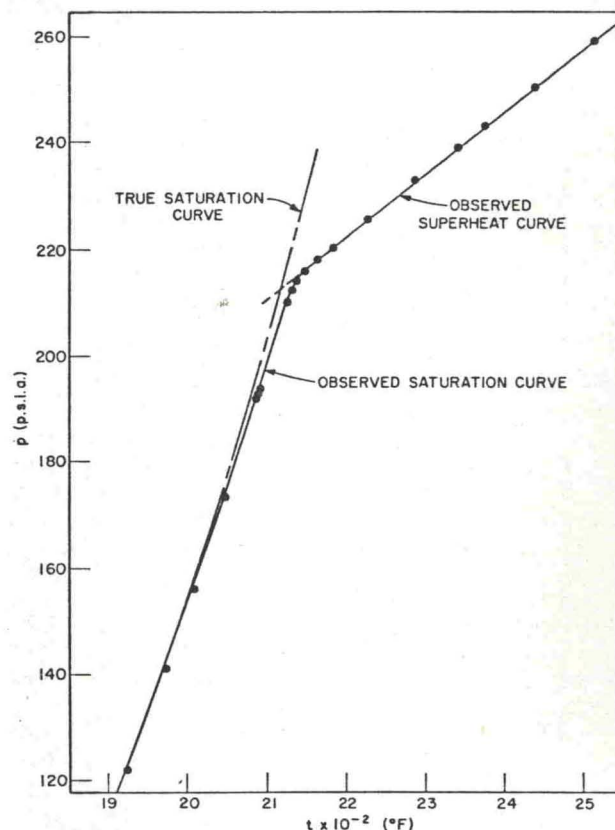


Figure 3. Pressure and temperature observations on superheated potassium vapor

Figure 4. Phenomenon at intersection of saturation and superheat curves
Illustrated with experiment 10

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

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

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 $\pm 0.1\%$, 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,

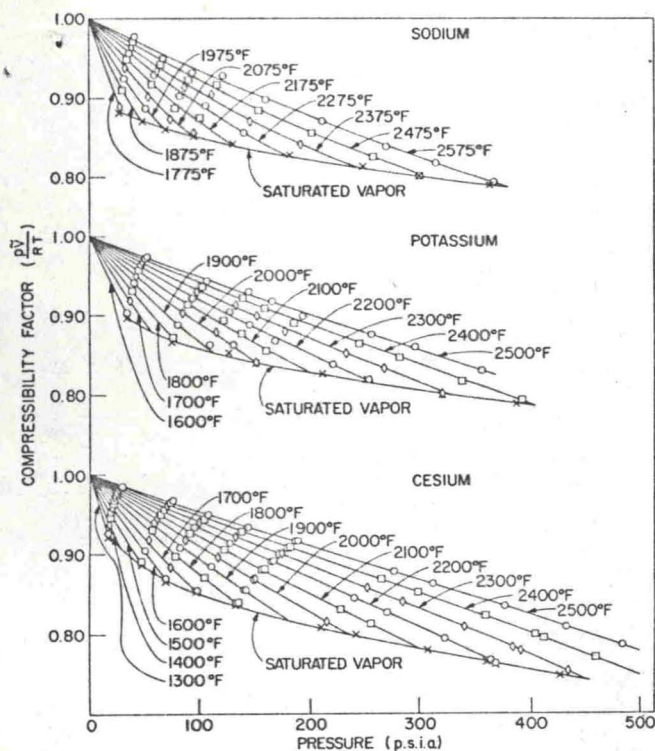


Figure 5. Compressibility factor-pressure diagrams for sodium, potassium, and cesium

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 $\pm 0.44\%$ for sodium, ± 0.26 to $\pm 0.35\%$ for potassium, and ± 0.25 to $\pm 0.28\%$ 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)

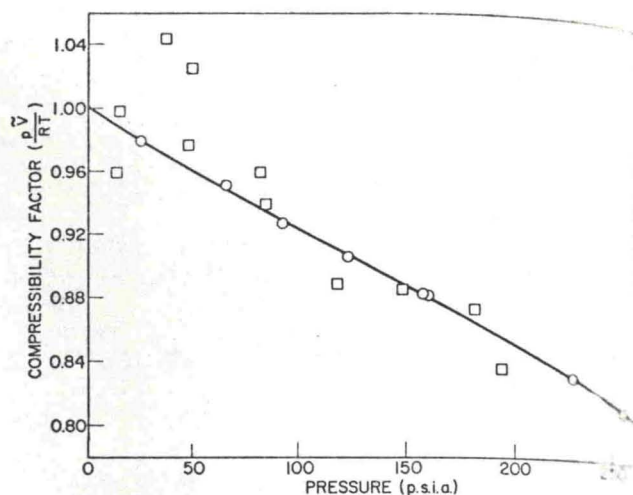


Figure 6. Comparison of observed compressibilities for cesium with those of Tepper at 2096° F.

○ Tepper
□ This work

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.

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 overall 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 $\pm 1.8\%$, 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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