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THE HIGH TEMPERATURE VAPOR PRESSURE AND THE CRITICAL POINT OF POTASSIUM

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ABSTRACT

The vapor pressure of potassium was experimentally determined from 2100 F up to its critical temperature. An empirical equation of the form $\ln P = A + B/T + C \ln T + DT^{1.5}$ was found to best fit the data. A critical pressure of 2378.2 ± 4.0 psia $(161.79 \pm 0.27$ ata) was measured. The corresponding critical temperature, extrapolated from the pressure-temperature curve, is 4105.4 ± 5 R $(2280.8 \pm 3$ K).

The technique employed was the pressure tube method developed earlier in this laboratory and used for determining the vapor pressure of rubidium and cesium. This method measures the critical pressure directly, as well as the vapor pressure at lower temperatures.

INTRODUCTION

Potassium has been studied as a nuclear reactor coolant and as a Rankine cycle working fluid for space power plants. For design and optimization of such uses, the vapor pressure is needed up to high temperatures, and preferably up to the critical point. In addition, critical point properties are useful in correlating and in predicting other properties. Finally, the family of the alkali metals provides a sequence of metals of graduated properties with which corresponding states can be compared and the nature of the liquid state studied.

Accordingly, the vapor pressure and critical point of potassium were measured by the "pressure tube" method, devised and initially employed with cesium (1-3) and rubidium (4,5) in this laboratory.

APPARATUS

The equipment employed with potassium (Fig 1) used the same concept as earlier of a small-bore "pressure tube" closed at one end and connected at the other to a liquid injection and high pressure measuring system. As before, pure dodecane was used above the alkali metal to force it n the pressure tube and to transmit the erated pressure to the gauges. Also ssure was read by a 3000 psi Heise gauge (6) and a 5000 psi CEC (7) transducer,

both calibrated with a dead weight gauge.

However, substantial improvements were adopted for this study. The pressure tube, including the closed tip, was now made of chemically vapor-deposited tungsten in one piece, 0.10 in. ID x 0.34 in. OD x 15 in. long (8). The open end was then centerless ground to 5/16 in. OD for a Gyrolok coupling to the system. Another key improvement was the use of a "displacement valve" or injector, a high pressure valve having a 3/8 in. diameter valve stem with a low-leakage Teflon cylindrical or Viton O-ring packing (9). The seat was drilled out to permit a longer stem travel, and the valve handle was fitted with a pointer and a scale graduated in hundredths of a turn. An additional injector was made from a high pressure stainless steel bellows (10) fitted with a close-pitch compression screw, also with a pointer and scale. It was too "soft," or compressible (high dV/dP at constant setting), to use or to leave in the active system while determining a vapor pressure, but was helpful for transferring substantial amounts of dodecane into or out of the system when necessary, then shut off.

The tip temperature was given by four W-5% Re/W-26% Re pairs of 0.010 in. bare thermocouple wires (11) with MgO sleeves1 (12). Two more thermocouples 0.5 and 1.0 in. away verified the positive temperature gradient towards the tip. The calibration provided every 200 F by the manufacturer was fitted by Least Squares with a cubic equation in temperature. The consensus is that this thermocouple wire does not drift in calibration with moderate times. At least over the several days required by each group of runs, this was verified by the good agreement among early and late points of P vs T.

Welding of tungsten tends to initiate grain growth and brittleness. Accordingly, the thermocouple wires were not welded together, nor to the pressure tube. Instead, the 8 tip wires were placed alternating in composition around the tip, leading axially away from the tube, then firmly tied down

MASTER

1Single sleeves, or double sleeves with both wires of the same composition, were employed, to avoid possible cross-conduction error (13)

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by several turns of 0.003 in. tungsten wire with its ends twisted tightly together. This arrangement substantially transferred the effective hot junctions to the contacts between the thermocouple wires and the pressure tube, calculated to be well within 1 F from the actual inner tip temperature. It also facilitated utilizing every wire that remained if one or more of the wires should become open-circuited, or picking a pair of spaced wires as a monitor couple, since each wire composition led to its own selector switch, and any one wire of each composition could be employed. In the C-runs thermocouples were read digitally (14) for speed and steadiness, and verified with a precision potentiometer at intervals. The furnace (15) was rated at 16 KVA and 2500 C and employed a 1.5 in. ID graphite tube heater 15 in. long, in an argon atmosphere. A thyristor SCR with phase angle control (16), employing a Dekapot working vs load IR drop, yielded very steady and finely controllable furnace temperatures.

Downward insertion of the pressure tube into the furnace was employed, as with Cs and Rb, to minimize likelihood of interference of possible inert gas left in the system with the vapor space at the tip. The possible disadvantage of instability in the observed pressure, due to liquid falling at the interface, was only observed in 3 runs (C-4,11,12) and did not cause disagreement between these break points and the vapor pressure correlating equations.

Experimental Procedure

The system (Fig 1) was first evacuated, then filled with 99.995% argon and reevacuated, several times. Then the pressure tube section was shut off and charged with 10 g of molten potassium (Table I), filling it and part of the SS tubing above it. Keeping the K molten, dodecane in the reservoir was deaerated by bubbling argon, the system reevacuated, and the dodecane passed downwards, completely filling the remaining system space. By passing DC along the SS tube and heating it with a Bunsen burner until a sharp IR break in the tubing was obtained, wetting of the tubing by the K was achieved and the location of the interface verified.

During charging and at all later times it is necessary to prevent penetration of the oil down into the K, where on later high temperature runs it would crack thermally and plug the pressure tube. This can be achieved by keeping the K molten by a low furnace power and heater tapes on the adjacent SS tube. For shutdowns it is necessary to cool and freeze the K sequentially from the pressuretube tip to the interface in the adjacent tube, avoiding freeze cracks. Remelting for later runs is done in the reverse sequence. Thus the plugs encountered previously with Cs and Rb, and after runs A and B, causing the termination of those runs, can be avoided.
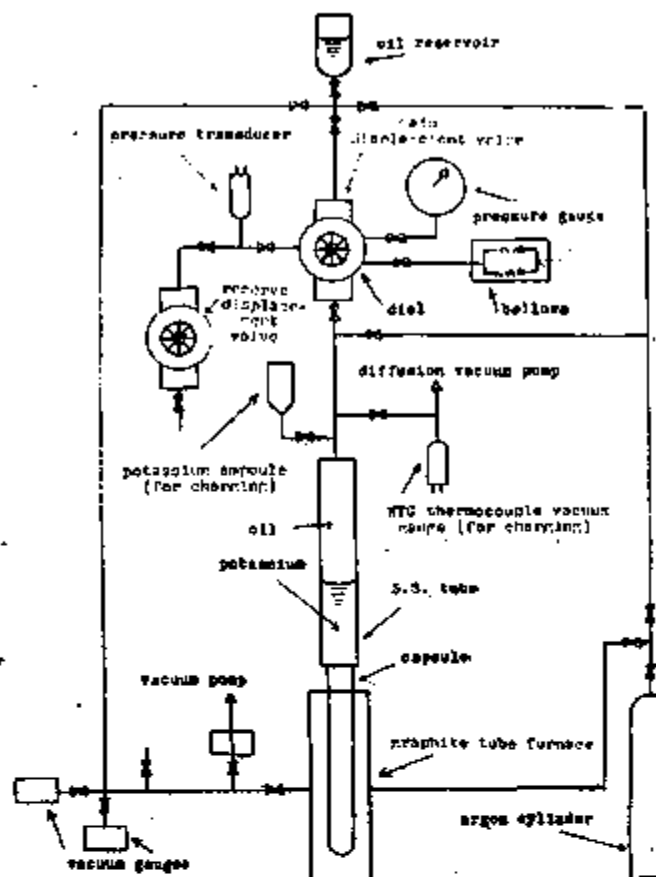
VAPOR PRESSURE

To obtain vapor pressure data, furnace power was adjusted until a steady tip temperature was observed in the desired temperature range. The bellows was then used to introduce or remove oil, so as to adjust the system pressure to about 100 psi below the expected vapor pressure with the injector stem at its outermost position. This ensured en adequate but not excessive vapor space at the tip of the pressure tube to complete a curve without further K addition. The K vapor-liquid interface was now slowly forced towards the tip by turning the injector handle inwards in small increments. This basically reduces the total system volume, and is equivalent to injecting K into a constant volume apparatus.

The vapor-liquid interface encounters rising temperatures as it moves towards the tip. The pressure inside the apparatus is seen to rise instantly to a new value with each small increment injected, which is the saturation vapor pressure at the local pressure tube temperature where the interface happens to be located. Thus, the pressure increase follows the temperature gradient along the pressure tube. After the liquid completely fills the tube, the pressure increases much more rapidly due to the greater "hardness" of a completely liquid-filled system. For each run the output of the pressure transducer was plotted on a recorder, and the Heise gauge reading and

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TABLE I
ANALYSIS PROVIDED FOR THE "HIGH PURITY POTASSIUM" SUPPLIED IN GLASS CAPSULES BY MSA RESEARCH, INC.

Si	25	ppm
Na	15	"
Ca	8	"
Mg	2	"
Mn	1	"
B,Zr	<10	" each
Fe,Co,Sn,Pb,Cr,Ti,Ni	< 5	"
Mo,Ba	< 3	" "
Al	< 2	"
Cu,V,Be,Ag,Sr	< 1	" "
O	<50	"
K (guaranteed)	>99.95%	

tip thermocouple voltages written on the chart at the correct time. Since a uniform time interval was employed for each point, a direct plot was obtained on which a preliminary observation could be made of the break. However, the Heise gauge readings were considered more reliable, and were employed in the final plots, e.g. Figs 2-4.
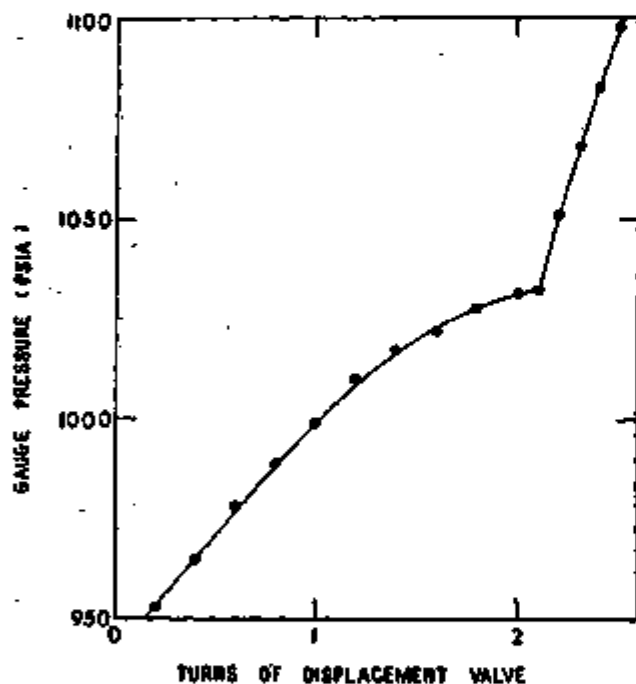

Fig.2   Run B4 (Subcritical)

Tip temperature: 3389.69 R
Break Pressure :   1032.34 psia

The two branches of each plot were then extended by straight-edges or French curves to their intersection. A correction for hydrostatic head of the gauge center over the pressure tube tip was added, and the tip temperature was obtained from the thermocouple wire correlation, using the average of the tip thermocouple voltages, after eliminating any that might have fallen out of general agreement with the others. A typical high temperature break is shown in

Fig 2. The procedure was continued for a number of volume and pressure increments beyond the break in the P-V curve, then the injector valve stem was screwed out and the procedure repeated at a new tip temperature.

CRITICAL PRESSURE

In a series of runs at increasing temperatures, eventually the pressure tube tip reaches and exceeds the critical temperature, T_c. In this situation, some point along the pressure tube, slightly above the tip, has exactly reached T_c. When the liquid-vapor interface reaches this position a change suddenly occurs: this interface disappears, and all of the fluid down to the tip changes from subcritical vapor to supercritical fluid. Experimentally it is found that a break, though less sharp, still occurs in the P-V curves. The break is evidently obtained at this location, namely at the critical pressure, P_c, which is thus observable, and at T_c, which is below T but is not determinable from the test alone, since neither the location of the interface nor the exact temperature distribution along the tube is known. P_c is verifiable by other runs at other high tip temperatures, which are found to show their breaks still at the same pressure, within a relatively high order of reproducibility for these rather extreme conditions.

Six points with supercritical tip temperatures were obtained, as listed in Table II, with widely different T, but P_c within a spread of 0.3%. Figs 3 and 4 show typical supercritical runs. An interesting difference is that Fig 3 shows an increase in slope at the break, as with the subcritical
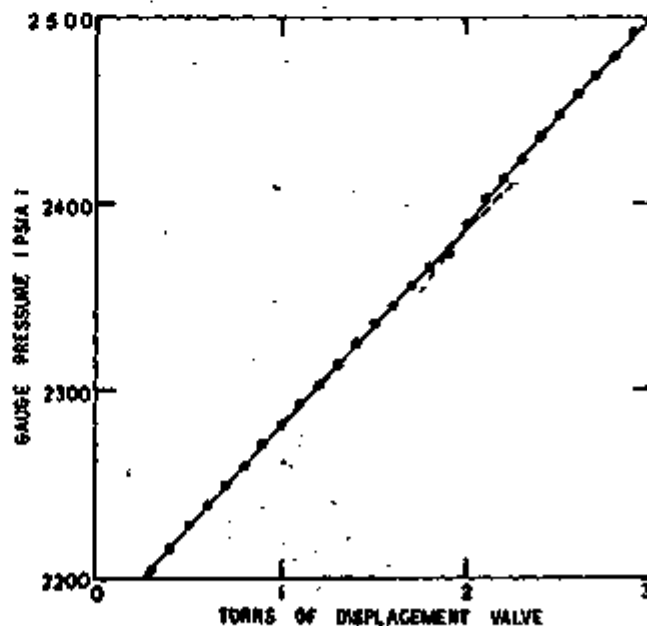

Fig.3   Run B16

Tip Temperature: 4347.18 R (Supercritical)
Break Pressure :   2381.00 psia (Critical)

runs, whereas Fig 4 shows a decrease in slope. On inspection, runs B-16 and 22, with tip superheats of 246 and 163 F, show increases. Runs C-8 and 18, with tip superheats of 36 and 19 F show decreases. Evidently high tip superheats cause slope increase and vice versa. Runs B-15 and 17, for which the tip thermocouples failed, show slope decreases, and presumably did have low tip temperatures. Interpolating
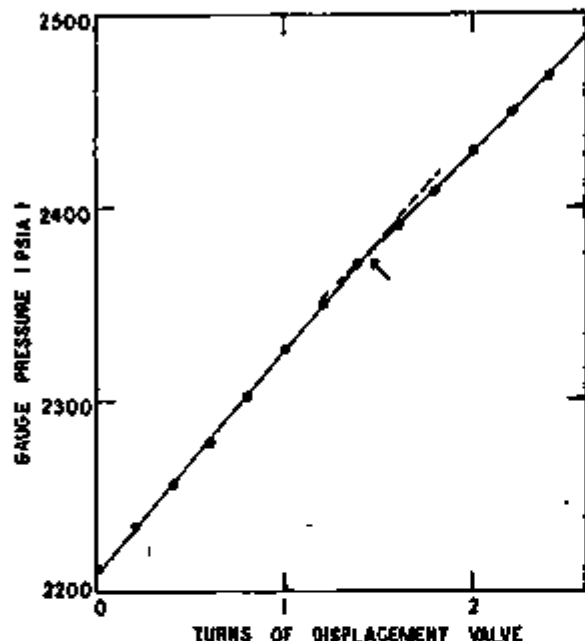
Fig 6. The tip temperatures are considered reproducible to ± 20 microvolts, or 2 F, with uncertainties in the calibration raising the standard error to about 5 F. The pressures are considered reproducible to within about 1 psi, and accurate to about 2.5 psi, which yields a standard error of about 3 psi, considering errors in the gauge and in the graphical intersection.

Fig.4   Run C14

Tip Temperature: 4119.7 R (Supercritical)
Break Pressure :   2373.52 psia (Critical)

on a plot of slope increase at the break vs $(T-T_c)$ gives tip superheats of some 41 and 28 F, respectively, for these runs. About 57 to 68 F is obtained as leading to no visible break. This observation might be verified theoretically, for a given tip temperature, by integrating along the tube to the tip, with an appropriate temperature distribution, and obtaining the integrated volume contraction for a small pressure increment. However, it has the practical result that if supercritical runs on occasion do not show a break with a particular substance in a given apparatus, one can probably overcome that difficulty by raising or lowering the tip temperature while still exceeding the critical temperature range.

Experimental Results

Three separate series of runs were carried out. Runs A and B yielded enough results for the thesis (17). Runs C were carried out as an added check on the prior results, and to obtain more data in the critical region.

The 44 points collected are given in Table II and, except for the 4 that were rejected for large deviations, are plotted in Fig 5, with the last 100 R enlarged in

Fig.5   Vapor pressure of potassium

Fig.6   Vapor pressure of potassium - critical region

CRITICAL PRESSURE

The critical pressure values in Table II yield a mean of 2378.2 psia with a standard deviation of 3.06 psia. An additional estimated uncertainty of 1.0 psia in the breakpoint and a gauge reading uncertainty estimated at 2.4 psia yield a standard error of P_c of 4.0 psia.

CRITICAL TEMPERATURE

Determining T_c requires extrapolating the vapor pressure as obtained from the experimental points to the accepted P_c of 2378.2 psia. This could be done by fitting

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TABLE II
EXPERIMENTAL DATA ON VAPOR PRESSURE AND CRITICAL PRESSURE
OF POTASSIUM, AND COMPARISON WITH CORRELATING EQUATIONS

(Date) Point No.	Experimental Data		Pressure by Correlating Equations			$(\Delta H^o_o)_v$
	Temperature (R)	Pressure (psia)	Eq 1 (psia)	Eq 2 (psia)	Eq 3 (psia)	Eq 4 (cal/g atom)
(12/71)						
A1	2558.79	203.40**			205.98	
A2	2732.49	311.77		318.78	313.40	23713.69
A3	2934.64	477.70		480.15	479.30	23767.98
A4	3093.49	644.20		639.21	642.96	23787.21
A5	3248.69	831.50		824.01	832.27	23820.28
A6	3373.84	1007.20		995.12	1006.29	23828.65
(3/72)						
B1	2727.39	309.20		315.26	309.80	23703.30
B2	3072.84	625.80		616.85	619.97	23761.73
B3	3221.39	800.07		789.33	796.84	23801.49
B4	3389.64	1032.34		1018.16	1029.61	23824.56
B5	3521.14	1229.60		1222.59	1235.23	23857.02
B6	3667.19	1488.24		1476.59	1487.20	23844.54
B7	3850.39	1843.20		1835.78	1836.46	23832.78
B8	3820.49	1776.15		1774.06	1777.05	23848.16
B9	2930.39	483.74		485.40	484.70	23765.60
B10	3387.09	1026.70		1014.42	1025.82	23830.01
B11	3721.39	1600.40		1578.12	1586.80	23818.16
B12	4026.39	2228.00	2209.56	2223.70	2203.85	23797.90
B13	4057.89	2264.00	2276.13	2297.56	2272.63	
B14	4134.69	2341.00**				
B15		2377.00*				
B16	4346.89	2381.00*				
B17		2382.00*				
B18	2790.39	356.24		360.53	356.24	23718.58
B19	3370.14	996.30		989.77	1000.87	23845.55
B20	3298.79	880.00**			899.67	
B21	4033.19	2206.00	2223.85	2239.53	2218.62	23830.22
B22	4263.79	2380.00*				
B23	3818.14	1766.05		1769.25	1772.42	23859.03
B24	4057.89	2211.00**			2272.67	23849.74
(5/72)						
C1	3574.75	1321.52		1312.51	1324.89	23852.92
C2	3519.39	1233.02		1219.73	1232.36	23840.27
C3	3710.95	1568.52		1558.26	1567.36	23844.79
C4	3839.06	1816.02		1812.25	1813.84	23841.75
C5	3936.37	2013.02		2020.04	2012.25	23841.23
C6	3993.16	2136.52	2140.35	2147.24	2132.25	23832.48
C7	4033.46	2223.52	2224.42	2240.16	2219.21	23830.22
C8	4136.42	2375.52*				
C9	4010.37	2179.52	2176.06	2186.66	2169.21	23821.46
C10	4062.54	2288.52	2286.04	2308.57	2282.85	23826.25
C11	4043.61	2248.52	2245.83	2263.91	2241.34	23824.93
C12	4080.10	2332.52	2323.63	2350.43	2321.63	23816.85
C13	4090.39	2342.52	2345.80	2375.16	2344.68	23830.52
C14	4119.71	2373.52*				

*Supercritical points not included in the curve-fit
**Other points not included in the curve-fit due to larger deviations from
smooth curve.

all of the points by least squares with a single equation of as many terms as is appropriate to minimize the standard deviation of the points from the equation. However, this would be imposing a single form of equation over the full temperature range, and in all probability increasing the deviation of the correlation from the higher points compared to a correlation limited to these points, which should have the greatest influence in extrapolating to obtain T_c.

Accordingly a simple Young's equation was fitted by least squares to only the top 10 points in Fig 6, yielding for P in psia and T in deg R:

$$\ln P = 11.524581 - 15,397.048/T \qquad (1)$$

with a standard deviation of 0.49%. Substituting $P=P_c=2378.2$ psia yields $T=T_c$ $=4105.4$ R $(2280.8$ K$)$, with a combined standard error of 5 R. This is accepted as the critical temperature of potassium from this program. A 3-term Kirchhoff equation was found not to yield a lower standard deviation than eq 1. It gave $T_c=4107.4$ R, which does not seem preferable to the straight-line result 4105.4 R, as a T_c lower than 4105.4, if different, might be expected

VAPOR PRESSURE

To fit the vapor pressure data over the full temperature range of this program, additional terms would be needed. Utilizing the full 34 accepted subcritical points, the following equations were developed:

Least Squares Kirchhoff equation:
$$\ln P = 6.54786-14614.9/T+0.576926 \ln T \qquad (2)$$

Eq 2 yielded a standard deviation of ln P of 0.0107, and an RMS error of the pressures themselves of 1.07%, and yielded $T_c=4091.6$ R at $P_c=2378.2$ psia. Noting the 14 R discrepancy in T_c, it is evident that this 3-term equation cannot fit these data, considering the wide temperature range they cover, as closely as would be desired. However, if only a 3-term equation is preferred and full closeness of fit is not required, eq 2 could be suitable, and simpler than using more terms.

Four-term Least Squares equation:
$$\ln P = 3.40397-15401.1/T+1.05145 \ln T$$
$$-2.38226 \times 10^{-6}T^{1.5} \qquad (3)$$

Eq 3 yielded a standard deviation of ln P of 0.0042, and an RMS error of the P values of 0.43%, and yielded $T_c=4105.5$ R. Eq 3 was established by applying an equation of this form to the 34 points with values of the exponent of the last term varying from 1 to 5 in increments of 0.5 and with the added constraint of passing through a set T_c from 4103 to 4107, also in increments of 0.5, at the established P_c of 2378.2 psia. Eq 3, then, has the exponent of the last term that best fits the 34 points and simultaneously yields $T_c=4105.5$ R, which of course is adequately close to the se-

lected 4105.4 R for all purposes. Actually, decreasing the set T_c slightly decreases the % total error further, to a minimum of 0.427% at $T_c = 4104.0$, the optimum exponent remaining at 1.5. It would seem that eq 3 best combines a fit of all the data points while weighting the important critical region.

Pressures calculated by the above equations 1-3 at the experimental temperatures of the accepted subcritical runs have been added in Table II for comparison. Eq 3 is seen to only once (point B-12) depart by over 1% from an experimental point, and most calculated values are within several tenths %. It thus seems appropriate for all purposes to employ values calculated by eq 3, and not to compare calculated vs experimental groups by temperature regions to obtain slight additional corrections for eq 3. Table III has been prepared from eq 3 for convenient interpolation.

COMPARISON WITH LITERATURE VALUES

Bowles (18) developed a refluxing apparatus superficially similar to that used in this work, in that it employed basically the same components. However, the capsule (i.e. pressure tube) was much larger, 0.7 in. ID. In addition, pains were taken to make it almost isothermal over its full length of 12 ins., with a slight temperature decrease of some 1 to 4 C going from bottom to top. The crucial difference was that each vapor pressure point was obtained at a constant level, with the capsule only partially filled and the potassium slowly vaporizing from the liquid pool, condensing higher up, and refluxing. Pressure was measured through the liquid phase, so bottom connection was required. The top center thermocouple was taken as giving the saturation temperature for the observed liquid pressure. This equipment was evidently carefully constructed but would seem to have had possible sources of error in the substantial vapor and liquid volumes in the large capsule, which might originate or obscure significant temperature variations, including colder spots in the wall of the vapor space, which might decrease the generated pressure. However, Bowles' results, which reach to about 200 F and 340 psi below the critical point, agree within about 0.5% with the present results, as seen in Fig 5 and Table IV. Thus, we recognize that he must have achieved so uniform a temperature, or in fact so consistent a low negative temperature gradient to the top, that his results agree with ours, which extrapolate to zero active volume. This agreement reinforces the validity of our pressure tube method and results, as well as of his own experimental care and results.

Freyland and Hensel (19) employed a method somewhat similar to Bowles, but with a smaller, thin-walled capsule, 26 mm tall and 6.85 mm in ID. They also utilized the capsule to determine electrical resistivity of the liquid K, and from the electrical

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TABLE III

INTERPOLATION TABLE FOR VAPOR PRESSURE OF POTASSIUM FROM 2000 R TO THE CRITICAL POINT

$$\ln P = 3.40397 - 15401.1/T + 1.05145 \ln T - 2.38226 \times 10^{-6} T^{1.5}$$

(P in lbs/sq in. abs; T in degrees R)

T	P	T	P	T	P	T	P
2000.0	32.53	2530.0	191.05	3060.0	605.05	3590.0	1351.02
2010.0	33.23	2540.0	196.15	3070.0	616.85	3600.0	1368.29
2020.0	35.17	2550.0	201.34	3080.0	627.93	3610.0	1385.57
2030.0	36.85	2560.0	206.62	3090.0	639.15	3620.0	1403.16
2040.0	38.39	2570.0	212.00	3100.0	650.32	3630.0	1420.76
2050.0	39.97	2580.0	217.47	3110.0	661.71	3640.0	1438.48
2060.0	41.50	2590.0	223.04	3120.0	673.23	3650.0	1456.31
2070.0	43.28	2600.0	228.71	3130.0	684.87	3660.0	1474.26
2080.0	45.01	2610.0	234.48	3140.0	696.63	3670.0	1492.31
2090.0	46.79	2620.0	240.35	3150.0	708.51	3680.0	1510.47
2100.0	48.62	2630.0	246.32	3160.0	720.51	3690.0	1528.75
2110.0	50.51	2640.0	252.39	3170.0	732.63	3700.0	1547.13
2120.0	52.46	2650.0	258.55	3180.0	744.88	3710.0	1565.63
2130.0	54.46	2660.0	264.83	3190.0	757.24	3720.0	1584.23
2140.0	56.51	2670.0	271.20	3200.0	769.73	3730.0	1602.94
2150.0	58.63	2680.0	277.58	3210.0	782.34	3740.0	1621.76
2160.0	60.30	2690.0	284.25	3220.0	795.08	3750.0	1640.68
2170.0	63.03	2700.0	290.95	3230.0	807.93	3760.0	1659.71
2180.0	65.32	2710.0	297.74	3240.0	820.91	3770.0	1678.85
2190.0	67.58	2720.0	304.64	3250.0	834.01	3780.0	1698.09
2200.0	70.09	2730.0	311.65	3260.0	847.23	3790.0	1717.44
2210.0	72.57	2740.0	318.76	3270.0	860.57	3800.0	1736.90
2220.0	75.17	2750.0	325.78	3280.0	874.04	3810.0	1756.45
2230.0	77.73	2760.0	333.21	3290.0	887.62	3820.0	1776.11
2240.0	80.40	2770.0	340.74	3300.0	901.33	3830.0	1795.88
2250.0	83.15	2780.0	349.29	3310.0	915.16	3840.0	1815.74
2260.0	85.96	2790.0	355.95	3320.0	929.11	3850.0	1835.71
2270.0	88.54	2800.0	363.71	3330.0	943.18	3860.0	1855.77
2280.0	91.79	2810.0	371.59	3340.0	957.38	3870.0	1875.94
2290.0	94.91	2820.0	379.58	3350.0	971.69	3880.0	1896.21
2300.0	97.90	2830.0	387.59	3360.0	986.13	3890.0	1916.57
2310.0	101.07	2840.0	395.90	3370.0	1000.68	3900.0	1937.04
2320.0	104.31	2850.0	404.23	3380.0	1015.36	3910.0	1957.60
2330.0	107.63	2860.0	412.57	3390.0	1030.16	3920.0	1978.26
2340.0	111.02	2870.0	421.23	3400.0	1045.07	3930.0	1999.02
2350.0	114.49	2880.0	429.90	3410.0	1060.11	3940.0	2019.87
2360.0	118.03	2890.0	438.58	3420.0	1075.27	3950.0	2040.81
2370.0	121.66	2900.0	447.59	3430.0	1090.55	3960.0	2061.85
2380.0	125.36	2910.0	456.60	3440.0	1105.94	3970.0	2082.99
2390.0	129.14	2920.0	465.73	3450.0	1121.45	3980.0	2104.22
2400.0	133.01	2930.0	474.98	3460.0	1137.09	3990.0	2125.54
2410.0	136.96	2940.0	484.34	3470.0	1152.94	4000.0	2146.95
2420.0	140.99	2950.0	493.32	3480.0	1168.72	4010.0	2168.45
2430.0	145.10	2960.0	503.62	3490.0	1184.71	4020.0	2190.04
2440.0	149.30	2970.0	513.14	3500.0	1200.81	4030.0	2211.73
2450.0	153.59	2980.0	522.58	3510.0	1217.04	4040.0	2233.50
2460.0	157.95	2990.0	532.93	3520.0	1233.38	4050.0	2255.36
2470.0	162.42	3000.0	543.01	3530.0	1249.84	4060.0	2277.30
2480.0	166.96	3010.0	553.29	3540.0	1266.41	4070.0	2299.34
2490.0	171.60	3020.0	563.51	3550.0	1283.10	4080.0	2321.46
2500.0	176.33	3030.0	573.64	3560.0	1299.91	4090.0	2343.66
2510.0	181.14	3040.0	584.49	3570.0	1316.83	4100.0	2365.75
2520.0	186.05	3050.0	595.16	3580.0	1333.87	4105.4	2378.17

resistance to verify that vapor phase was present in a vapor pressure determination. Their tests showing a substantial constancy of the temperature at the top of the capsule while refluxing isobarically at different rates seemed to confirm the merit, in the boiling method, of measuring condensing rather than boiling surface temperature. However, they selected as the critical point a condition of instability in the cell, which, as shown in Fig 5, is about 150 F and 70 psi too low, and, in fact, rather far from the vapor pressure curve. Furthermore, their vapor pressure data, as seen in Fig5,6 have a higher slope than ours, agreeing with eq 3 at approximately 2860 R and ranging from lower below that temperature up to 9.4% high at 3956 R, their supposed T_c.

It would seem that the main trouble is that with a wide vertical cell and a negative temperature gradient, instability is to be expected before the critical point is reached, and Bowles probably did not encounter it because his maximum temperature was somewhat lower and his temperature gradient and L/D ratio much smaller. It also seems probable that Freyland and Hensel at their higher temperatures would not have observed as good constancy of their condensing temperature with change of capsule temperature gradient as they did in the run reported at 23 bars (19). For a given capsule overall ΔT, the boil-up rate would no doubt increase with P (20), and very probably the condensing film ΔT would increase, and the surface temperature would have to decrease. Presence of any noncondensible gas would have a similar effect. These effects are both in the direction of the main discrepancy in their vapor pressure data. In particular, it may be that accurate critical property determinations cannot be dependably carried out in capsules with finite volumes of both liquid and vapor phase, and that extrapolation to the condition of a single phase, only locally at the critical point, as made use of in the "pressure tube" method here employed for P_c and T_c, and approximately in the "tilting capsule" method for ρ_c and T_c (21), is preferable.

Among the prior studies of the vapor pressure of potassium, that of Ewing et al (22) was the most complete and reached the highest temperature, 2836 R. Table IV shows that agreement with his equation is obtained at about 3200 R, his pressure being some 2.7% high at 4000 R. It is therefore undesirable to extrapolate his Kirchhoff-type equation beyond some 3200 R.

TABLE IV
COMPARISON OF CORRELATIONS FOR VAPOR PRESSURE OF POTASSIUM (PSIA)

°R	Eq 3	Bowles (18)	Ewing et al(22)
2400	(133.01)	130.14	127.67
2800	363.71	364.44	358.50
3200	769.73	774.60	(770.21)
3600	1368.29	1372.74	(1385.76)
4000	2146.95	2145.15	(2203.75)

These equations in psia and R are:
Bowles: $\ln P = 21.13050 - 19945.3/T - 1.02160 \ln T$
Ewing et al: $\ln P = 16.82326 - 18732.22/T - 0.53560 \ln T$

THERMODYNAMIC CONSISTENCY

As an independent verification of the internal consistency of the vapor pressure data, the "Third Law" check was applied(23). The heat of vaporization of the monomer at absolute zero was computed for each measured saturation point. The equation employed is:

$$(\Delta H_o^o)_V = -RT \ln p_{1s} - T\left[\left\{\left(\frac{h_T^o - h_c^o}{T}\right)^g - s_T^{o^g}\right\}(4) - \left\{\left(\frac{h_T^o - h_c^o}{T}\right)^1 - s_T^{o^1}\right\}\right]$$

where $p_{1s} = \dfrac{-1 + \sqrt{4KP_s + 1}}{2K}$ (5)

The vapor dimerization equilibrium constant K was obtained from Stull and Sinke (24) and the enthalpy and entropy functions from the formulae for $C_p(T)$ used by Ewing et al (25). The average $(\Delta H_o^o)_V$ was 22.267 Kcal/g atom, some 2% higher than 21.7 as calculated from low temperature measurements (26). In addition, there is a slight steady decrease in $(\Delta H_o^o)_V$ of 1% over the whole range of 2700 to 4100 R, with a standard deviation of 0.5% of the points from the best straight line. Accordingly, these vapor pressure values are well corroborated by this standard test.

Due to the uncertainties in the required extrapolations of the several thermodynamic functions to these considerably higher temperatures, it was also decided to determine the average $C_{p,L}$ which would eliminate the modest trend with temperature of $(\Delta H_o^o)_V$. It was found that a $C_{p,L}$ of 0.213 yielded an average $(\Delta H_o^o)_V$ of 23.816 Kcal/g atom with a standard deviation of 0.17%. Leaving out the 7 lowest temperature points, with presumably the least accuracy in vapor pressure, the average $(\Delta H_o^o)_V$ becomes 23.835 over the range of 3200 to 4100 R, with a standard deviation of only 0.05%. If these vapor pressure data are accorded greater accuracy than the extrapolation of $C_{p,L}$, it would be concluded

that a constant value of 0.213 cal/g deg K for $C_{p,L}$ is preferable to the function of in this high temperature range, even hough the $(\Delta H_0^0)_V$ obtained is some 10% higher than reported by Evans et al (26).

NOMENCLATURE

$C_{p,L}$ C_p of saturated liquid, cal/g K
T   Equilibrium temperature corresponding to P, deg R = 459.7+F

$(\Delta H_0^0)_V$ Standard heat of vaporization of potassium monomer at 0 R, cal/g atom

K   Equilibrium constant of dimerization, atm^{-1}

P_s, P Vapor pressure of saturated liquid, atm

P_{1s} Partial pressure of monomeric potassium, atm

(h_T^0) Enthalpy at standard state, BTU/lb

s_T^0 Entropy at standard state, BTU/lb R
R   Gas constant

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