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VAPOR PRESSURE OF POTASSIUM TO 2170° K

by Kenneth J. Bowles
Lewis Research Center
Cleveland, Ohio



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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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ABSTRACT

A static capsule method was used to measure the vapor pressure of potassium from 945° to 2170° K. The resulting Kirchhoff-type vapor-pressure equation is

$$\log \frac{p}{p_0} = 7.74887 - \frac{4812.30}{T} - 1.02160 \log T$$

where p is the vapor pressure in N/m^2 , p_0 is atmospheric pressure at sea level ($1.01325 \times 10^5 \text{ N/m}^2$), and T is the absolute temperature in °K. The standard deviation in pressure is ± 1.23 percent. Data calculated from this equation were pooled with data calculated from potassium-vapor-pressure equations determined previously in four independent studies. The pooled equation is used as a standard curve against which all data are compared.

VAPOR PRESSURE OF POTASSIUM TO 2170⁰ K

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SUMMARY

The vapor pressure of potassium was measured over a temperature range from 945⁰ to 2170⁰ K by using a static capsule method. The data were fitted to the Kirchhoff-type vapor-pressure relation with the resulting equation being

$$\log \frac{p}{p_0} = 7.74887 - \frac{4812.30}{T} - 1.02160 \log T$$

where p is the vapor pressure in newtons per square meter, p_0 is atmospheric pressure at sea level ($1.01325 \times 10^5 \text{ N/m}^2$), and T is the absolute temperature in ⁰K. The standard deviation in pressure p is ± 1.23 percent. Data calculated from this equation were pooled with data calculated from potassium vapor-pressure equations determined previously in four other independent studies. The pooled equation is used as the standard curve against which all data are compared.

INTRODUCTION

Potassium is presently under consideration as a working fluid for advanced space power systems. The use of potassium as a thermodynamic working fluid at temperatures in excess of 1425⁰ K has created a need for the accurate measurement of high-temperature properties of the fluid. The vapor-pressure curve is considered to be one of the significant items of thermodynamic information for the design of space power systems. In addition to the engineering requirements for vapor-pressure information, the theoretical study of the liquid state of metals will benefit greatly from such high-temperature experimental investigations. To date, only the metal mercury has been studied over its complete liquid range.

Several investigators, using different experimental procedures, have determined vapor-pressure curves for potassium in various temperature ranges above the normal

boiling point (ref. 1, 860^o to 1280^o K; ref. 2, 753^o to 1423^o K; ref. 3, 1065^o to 1500^o K; and ref. 4, 1030^o to 1585^o K). Above 1200^o K there is relatively good agreement of the data of these four investigators, but at 1000^o K differences as great as 8 percent in pressure exist. Vapor-pressure data obtained by arbitrarily extrapolating any of these experimentally developed equations outside of the experimental range could result in unusually large deviations from the actual vapor pressure of potassium. Grachev and Kirillov (ref. 5) have also measured the vapor pressure of potassium to 1550^o K; however, their data deviate considerably from the data of other investigators.

A static capsule method, developed at the Lewis Research Center and previously used to measure the vapor pressure of sodium over the temperature range 1072^o to 2150^o K (ref. 6), was used to measure the vapor pressure of potassium. The results of the experimental investigation for potassium are presented herein and compared with the results of other investigators.

EXPERIMENT

The vapor pressure of potassium was determined by heating a quantity of potassium in a closed capsule and measuring the pressure produced at various temperatures.

Apparatus

The apparatus for measuring the vapor pressure of potassium has previously been described in detail in reference 6. The apparatus, without the heater and heat-shield assembly, is shown in figure 1.

A tantalum - 10-percent-tungsten alloy capsule contains the potassium sample being heated. The saturation pressures being generated within the capsule are transmitted from the capsule to the pressure transducers through liquid potassium inside small-bore tubing. Hot silicone oil (373^o K) is pumped through the pressure transducer case and into the cooler. The hot oil keeps the potassium pressure transmission tubing at a temperature above the melting point of potassium. It also cools the lower end of the hollow stem at the end of the capsule.

Procedure

The entire system was evacuated to a pressure of 10^{-6} torr (1.333×10^{-4} N/m²). (The capsule evacuation line, shown in fig. 1, is connected into the same vacuum pump

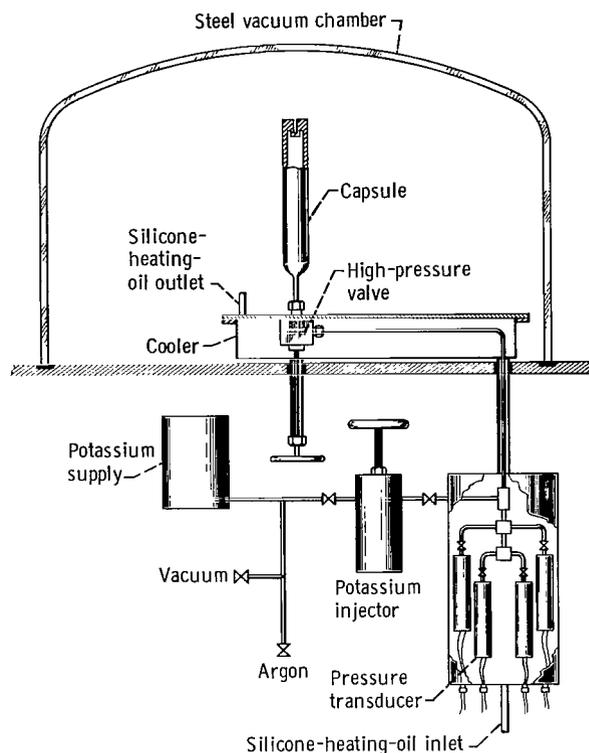


Figure 1. - Apparatus for measuring high-temperature vapor pressure of potassium.

manifold through which the main vacuum chamber is evacuated.) The capsule, storage tank, and interconnecting tubing were baked out at a minimum temperature of 423° K for a period of 8 hours. After the bake-out period was complete, as determined by the bell-jar pressure, potassium was transferred from the storage tank to the evacuated injector. A measured amount of potassium was then injected into the capsule (also under a vacuum) and the capsule was heated to various test temperatures. The saturation pressures were recorded after a sufficient time had elapsed to allow the capsule and its contents to reach an equilibrium temperature. The time required to reach equilibrium varied from 60 minutes at 1000° K to 15 minutes at 2170° K. The vapor-pressure data obtained are presented in table I.

Temperature measurements. - Platinum - platinum-13-percent-rhodium (Pt - Pt-13Rh) thermocouples were used for the temperature readings in runs 1 and 2 (table I). These thermocouples were calibrated with an NBS secondary standard Pt - Pt-13Rh thermocouple. The estimated error in the temperature readings in runs 1 and 2 is $\pm 0.5^{\circ}$ K. Tungsten-5-percent-rhenium - tungsten-26-percent-rhenium (W-5Re - W-26Re)

TABLE I. - POTASSIUM VAPOR PRESSURES

Absolute temperature, T, °K	Reciprocal absolute temperature, T ⁻¹ , °K ⁻¹	Vapor pressure, p		Absolute temperature, T, °K	Reciprocal absolute temperature, T ⁻¹ , °K ⁻¹	Vapor pressure, p		Absolute temperature, T, °K	Reciprocal absolute temperature, T ⁻¹ , °K ⁻¹	Vapor pressure, p	
		atm	N/m ²			atm	N/m ²			atm	N/m ²
Run 1				Run 3				Run 4			
945.1	10.581×10 ⁻⁴	0.4116	0.4170×10 ⁵	1115.4	8.965×10 ⁻⁴	2.1429	2.1713×10 ⁵	1553.6	6.437×10 ⁻⁴	24.7279	25.0555×10 ⁵
1059.8	9.436	1.3330	1.3506	1178.4	8.486	3.4626	3.5085	1653.1	6.049	35.6938	36.1667
1159.4	8.625	2.9558	2.9950	1266.6	7.895	6.0000	6.0795	1723.6	5.802	43.9932	44.5761
1240.3	8.063	5.1292	5.1972	1341.6	7.454	9.2857	9.4087	1769.5	5.651	51.1700	51.8480
1320.2	7.575	8.2585	8.3679	1416.9	7.058	13.5442	13.7237	1803.7	5.544	56.1360	56.8798
Run 2				1457.7	6.860	16.3946	16.6118	1838.3	5.440	61.7619	62.5802
1001.0	9.990×10 ⁻⁴	0.7211	0.7306×10 ⁵	1543.8	6.478	23.7687	24.0836	1875.0	5.333	68.6870	69.5971
1126.5	8.877	2.2993	2.3298	1611.6	6.205	30.6734	31.0798	1922.9	5.200	78.3129	79.3505
1198.7	8.342	3.9864	4.0392	1653.0	6.050	35.0952	35.5602	1958.1	5.107	85.6258	86.7603
1291.4	7.744	6.9898	7.0824	1706.7	5.859	42.1497	42.7082	2003.4	4.992	95.3061	96.5689
1343.9	7.441	9.4115	9.5362	1804.5	5.542	55.8639	56.6041	2072.7	4.825	111.6122	113.0911
1388.7	7.200	11.8639	12.0211	1861.8	5.371	65.6939	66.5643	Run 5			
1427.6	7.005	14.3503	14.5404	1915.3	5.221	76.5442	77.5584	1875.6	5.332×10 ⁻⁴	68.5034	69.4111×10 ⁵
1448.0	6.906	15.7551	15.9638	1987.1	5.032	91.4762	92.6882	1989.5	5.026	41.3265	41.8741
1466.8	6.818	17.1598	17.3872	2038.9	4.905	102.7007	104.0615	2029.6	4.927	100.4898	101.8213
1496.5	6.682	19.4966	19.7549					2078.8	4.810	111.4900	112.9672
1545.3	6.471	23.6735	23.9872					2124.1	4.708	119.8571	121.4452
1587.0	6.301	28.5034	28.8811					2169.0	4.610	131.8027	133.5491
1604.3	6.233	29.2857	29.6737								
1625.7	6.151	31.9048	32.3275								

thermocouples were used to measure the temperature in runs 3, 4, and 5. In run 2, a W-5Re - W-26Re thermocouple was calibrated against one of the Pt - Pt-13Rh thermocouples spotwelded onto the capsule wall. The calibration was run over a temperature range from 1100^o to 1600^o K. The data obtained from this calibration run deviated by no more than 0.019 millivolt from the calibration data received from the thermocouple wire manufacturer. Over this temperature range this deviation represents a maximum of 1.2^o K. The calibration data obtained in run 2 were used to correct those temperature measurements below 1600^o K in runs 3 and 4. The estimated accuracy of these temperature measurements is $\pm 1^{\circ}$ K. For temperatures above 1600^o K, the calibration data supplied with the thermocouple wire were used. The estimated error of measurement for these temperatures is $\pm 4^{\circ}$ K.

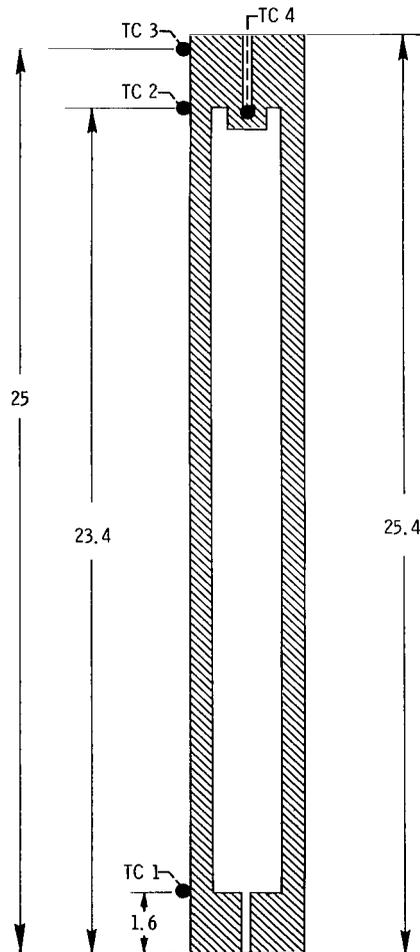


Figure 2. - Thermocouple (TC) locations on vapor-pressure capsule. Dimensions in centimeters.

A diagram of the capsule and thermocouple positions is shown in figure 2. The thermocouple located in the thermowell at the top of the capsule (TC 4, fig. 2) was taken to be that thermocouple which indicated saturation temperature. A slight temperature differential (decrease in temperature from the bottom of the capsule to the top) was designed into the heater - radiation-shield assembly. Temperature profiles of the capsule at various temperature levels are given in table II. Thermocouples were attached only to the ends of the capsule since temperature profiles determined previously in reference 6 showed that temperatures in the central portion of the capsule were within the temperature extremes measured at the ends of the capsule. A slight temperature differential along the length of the capsule is desirable in order to control the location of the coolest surface in the vapor space so that the saturation temperature may be measured at that location. It is also desirable to maintain the temperature differential at a small magnitude to minimize superheating of the liquid phase which could result in cycling of the temperature and pressure due to "slugging" of the liquid to the top of the capsule.

TABLE II. - TEMPERATURE PROFILES OF
VAPOR-PRESSURE CAPSULE

Thermocouple	Temperature, °K					
1	1096.6	1321.8	1527.3	1688.7	1898.2	2019.5
2	1096.2	1321.3	1524.2	1685.8	1892.1	2015.9
3	1093.0	1318.0	1520.2	1683.0	1887.7	2009.9
4	1095.3	1321.0	1523.8	1685.8	1894.2	2018.1

Pressure measurements. - The vapor-pressure measurements were made with two pressure transducers that covered a range from 0 to 238 atmospheres (0 to 241.15×10^5 N/m²) in two overlapping ranges: (1) 0 to 34 atmospheres (0 to 34.45×10^5 N/m²), and (2) 0 to 238 atmospheres (0 to 241.15×10^5 N/m²). Each of these transducers was cali-

brated over its pressure range in position within the vapor pressure rig. All calibration pressures and experimental vapor pressures were measured at a transducer temperature of 366.5° K. The calibrating gages were three Bourdon tube test gages covering the ranges 0 to 13.6 atmospheres (0 to 13.78×10^5 N/m²), 0 to 68.0 atmospheres (0 to 68.90 N/m²), and 0 to 680 atmospheres (0 to 689.0×10^5 N/m²). The estimated accuracy of the pressure measurements in these runs is 0.018 atmosphere (1.8×10^3 N/m²) for pressures up to 20.4 atmospheres (20.7×10^5 N/m²), 0.054 atmosphere (5.47×10^3 N/m²) for pressures between 20.4 and 34.0 atmospheres (20.7×10^5 and 34.45×10^5 N/m²), 0.17 atmosphere (1.7×10^5 N/m²) for pressures from 34.0 to 95.0 atmospheres (34.45×10^5 to 96.26×10^5 N/m²), and 0.5 atmosphere (5.07×10^4 N/m²) for pressures above 95.0 atmospheres (96.26×10^5 N/m²).

Potassium purification. - Analyses of the potassium used in this investigation showed an oxygen content of less than 30 ppm of oxygen. The fluid used was vacuum-distilled at the Lewis Research Center and is considered to be of adequate purity for this investigation. All potassium transfer operations were performed under vacuum.

RESULTS AND DISCUSSION

During the series of five vapor-pressure runs, a total of 51 data points were recorded. The results of these vapor-pressure runs are listed in table I. The data were fitted to the three-constant Kirchoff equation by the method of least squares and are represented by the equation

$$\log \frac{p}{p_0} = 7.74887 - \frac{4812.30}{T} - 1.02160 \log T$$

where p is the vapor pressure in newtons per square meter, p_0 is atmospheric pressure at sea level (1.01325×10^5 N/m²), and T is the absolute temperature in °K. The standard deviation in pressure p of the data from the equation is calculated to be ± 1.23 percent. A semilog plot of this equation as p/p_0 against T^{-1} is shown in figure 3.

Prior to the start of run 4, 25 percent more potassium was injected into the capsule to verify the existence of true liquid-vapor equilibrium over the entire range of this investigation. There is no noticeable deviation between the vapor-pressure curve calculated from runs 1, 2, and 3 and the data points of run 4.

The depression of the vapor pressure of potassium due to the impurities in the potassium, assuming that Raoult's law is obeyed, is calculated to be negligible. Dissolution of the container material, mostly tantalum, is dependent on the amount of oxygen in the potassium metal and in the container material (ref. 7). The maximum depression of

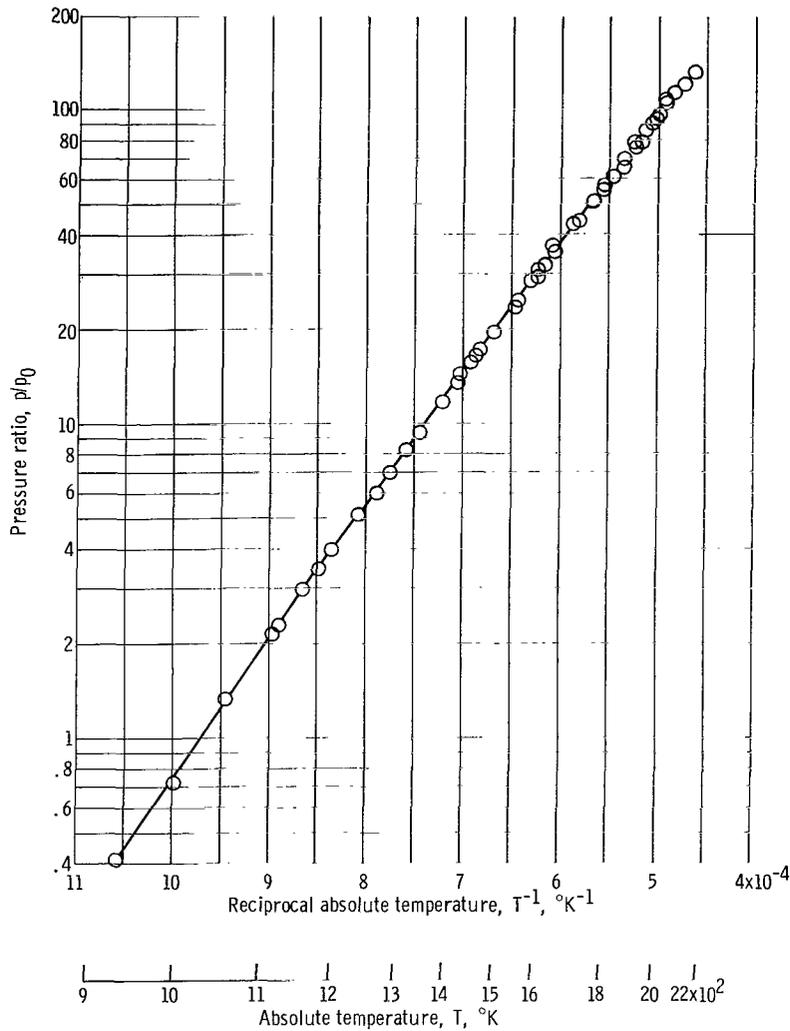


Figure 3. - Vapor pressure of potassium at temperatures from 945° to 2170° K.

the vapor pressure of potassium, caused by a potassium-oxygen-tantalum reaction, is calculated to be less than 0.25 percent at the maximum temperature of this study.

An analysis was made to determine the effect of the instrumentation inaccuracies on the deviation of the experimental data from absolute or true values of the vapor-pressure data. Of the 51 data points obtained, only 5 fell a significant distance outside these calculated deviations built into the experiment by the instrumentation. Two other data points fell approximately at the limits of the calculated deviations, and all the remaining data points were well within these limits.

As a means of comparing the vapor-pressure equations determined from the data of this study with vapor-pressure equations of other investigators, data calculated from the equation of this investigation were pooled with calculated data from the equations of references 1 to 4 to determine a single median curve. Each vapor-pressure equation was solved for p at integral values of $T^{-1} \times 10^{-4} \text{ } ^\circ\text{K}^{-1}$ over its experimental temperature range of study.

Figure 4 shows a graphical comparison of the various computed vapor-pressure values. The abscissa is shown as temperature in $^\circ\text{K}$, and the ordinate is shown as $[(p_p - p)/p_p] \times 100$, where p_p denotes the pooled vapor-pressure value. The solid line curve for each investigator is shown to extend over the range of the data from which the mathematical vapor-pressure relation was derived. The data of reference 5 are not shown since they fall outside the ordinate limits of this figure.

A low-temperature extrapolation of data points calculated from the vapor-pressure equation developed in this investigation is shown as a dashed line in figure 4. The pooled equation is also extrapolated to $T^{-1} = 13 \times 10^{-4} \text{ } ^\circ\text{K}^{-1}$ (770°K). These extrapolated data points are compared with low-temperature data calculated from a thermodynamic study (ref. 8) of the experimental data of several investigators.

Data calculated from the smoothed vapor-pressure curve of reference 9 are also shown in figure 4. In reference 9 the vapor-pressure equation was developed by combining the vapor-pressure data of selected investigators in a least squares fit to a three-constant equation. This vapor-pressure equation of reference 9 differs only slightly from the pooled equation of this report. A divergence at the low temperatures is apparent,

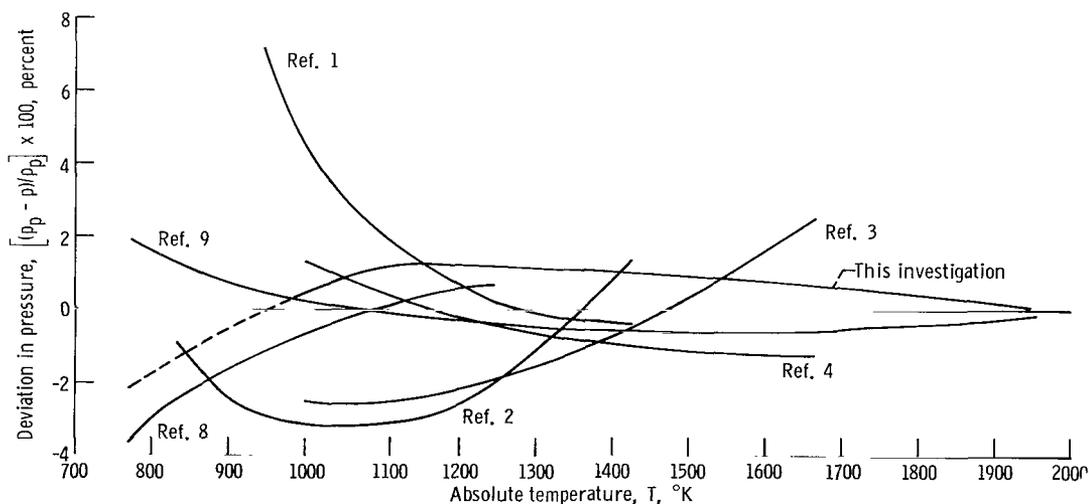


Figure 4. - Comparison of vapor-pressure equations for potassium.

although the maximum is only about 2 percent at 770^o K.

In the temperature range above 1000^o K the vapor-pressure curves of reference 4 and of this investigation agree within 2.0 percent. Above 1100^o K the vapor-pressure equation of reference 1 also falls within this 2-percent range. Above 1100^o K there may be a systematic error, possibly caused by the difference in experimental equipment, between these three investigations. The low-temperature extrapolation of the vapor-pressure curve from this investigation agrees well with the calculated data of reference 8 and differs by an approximately constant percentage. The data of references 2 and 3 vary as much as 3 percent from the pooled equation of this investigation at temperatures near the normal boiling point of potassium.

SUMMARY OF RESULTS

A static capsule method was used to measure the vapor pressure of potassium at temperatures of 945^o to 2170^o K. The resulting data are represented by the equation

$$\log \frac{p}{p_0} = 7.74887 - \frac{4812.30}{T} - 1.02160 \log T$$

where p is the vapor pressure in newtons per square meter, p_0 is atmospheric pressure at sea level ($1.01325 \times 10^5 \text{ N/m}^2$), and T is the temperature in ^oK. The standard deviation of the experimental data from this equation is ± 1.23 percent. Calculated points from the equation, including extrapolated low-temperature vapor-pressure points, are in acceptable agreement with those of other investigators.

The results of this investigation have demonstrated the usefulness of the developed apparatus as a research tool for obtaining very high temperature vapor-pressure data for liquid alkali metals.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 12, 1968,
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