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The High Temperature Vapor Pressure
and the Critical Point of Potassium

by

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II. ABSTRACT

The vapor pressure of potassium was experimentally determined from 1600°F up to the critical point. An equation of the form $\ln P = A + B/T + C \ln T$ was found to fit the experimental data well, but addition of a fourth term D/T^2 further improved the fit considerably.

A novel design was employed in measuring the vapor pressure. A closed-end high pressure, small-bore tube partially filled with potassium is heated in a high temperature furnace. The liquid potassium is then forced, by compressing a bellows or turning a valve stem, to fill the small-bore, thick walled tube by small increments. The tip of this "capsule" is maintained at a constant temperature during the run. As the potassium is injected further and further, the liquid level passes through higher and higher temperatures, generating increasing vapor pressures. When the level reaches the tip of the tube no more vapor space remains, and a further liquid injection increases the observed pressure sharply. The saturation pressure corresponding to the observed temperature of the tip is indicated by the discontinuity in a curve of the pressure plotted against the motion of the bellows or turning of the valve stem. The tip temperature is then changed and another vapor pressure point is obtained.

This method provides a direct determination of the critical pressure, because at all tip temperatures higher than the critical temperature the same "break off pressure" is observed. This "break off" pressure, which is produced when the liquid level reaches the critical temperature in its travel along the bore of the tube, will evidently remain constant, independent of the tip temperature, and is the critical pressure.

III. INTRODUCTION

At the present time, due primarily to the development of nuclear reactors, the use of liquid metals has been emphasized considerably. The use of nuclear power and the corresponding development of higher temperature refractory alloys have caused a growing demand for high temperature working fluids. This is due to the increased thermal efficiencies of power cycles operating at higher boiler temperature.

There are three important conditions under which liquid metals are handled or used. The first is the common melting alloying of metals and their conveying to a suitable mold for casting and solidification. The second is the physical use of a metal in the liquid state, usually for heat-transfer purposes. The third is chemical use, in which the metal, usually sodium, is consumed in a reaction.

Uses of liquid metals evolving from their physical properties are relatively few as yet, but many proposed uses may be suggested. Recently, the liquid metals have become very attractive as coolants, or heat transport agents, particularly sodium for nuclear fast-breeder reactors. The liquid metal should have the following desirable properties, as far as possible: high heat transfer coefficients, chemical and radiation stability, non-corrosiveness of the usual strong and refractory metals, and low density. Potassium has also been suggested as a combined reactor coolant and Rankine cycle working fluid for space nuclear power plants.

Evidently the physical properties of the liquid metals have to be known before meaningful analyses and designs can be made. In particular, the principal thermodynamic properties must be known accurately, as other properties can be estimated once the primary properties, pressure, temperature, volume, and specific heat are measured.

Of comparable importance, both from a theoretical and an applied position, is the critical point of any substance. The critical point is that point on the thermodynamic surface of the substance where the liquid and vapor phases become identical. A characteristic of the critical point is that for values of either intensive property, temperature or pressure, above its critical value, it is impossible for two distinct phases to coexist.

Besides setting the maximum of the temperature range over which a substance can exist as a liquid, the critical point is of fundamental importance in the elucidation of the dynamic behavior of the liquid and gaseous states.

An adequate theory of the critical point is lacking. Mayer (1) applied the cluster theory of statistical mechanics to condensed systems and concluded that a critical region exists. Recent evidence (2), however, indicates that perhaps the Ising model (3), which predicts a smooth phase transition at the critical point, is more representative. Other evidence (4,5) points to a singularity at the critical point which implies that it is not analytic. Obviously, more experimental data must be obtained for temperatures close to the critical point.

It is, therefore, the purpose of this investigation to measure the saturated vapor pressure of potassium up to the critical point, and to establish its critical temperature and pressure.

IV. SUMMARY OF PREVIOUS WORK

A. Physical Property Data

The liquid metals have been investigated since the early days of the 1900's. The Liquid Metals Research Laboratory at Columbia University has been continuously obtaining liquid metal physical property data, and several other research laboratories have initiated alkali metal studies within the past decade under AEC, NASA, or Air Force sponsorship.

A number of investigators have published extensive data on the thermodynamic properties of alkali metals to maximum temperatures of 2000°F to 2500°F. In addition, vapor pressure data to about 3000°F have been reported by Bohdansky (6) on lithium, Bowles (47) and Heime1 (8) reported vapor pressure data on potassium up to 3446°F and 3280°F respectively, and Bowles (7) has measured the vapor pressure of sodium to 3400°F.

Several other investigators, using different experimental procedures, have determined vapor-pressure curves for potassium in various temperature ranges above the normal boiling point. Above 1200°K there is relatively good agreement of the data obtained, but at 1000°K differences as great as 8 percent in pressure exist. Grachev and Kirillov (9) have also measured the vapor pressure of potassium to 1550°K; however, their data deviate considerably from the data of other investigators. The apparatus for measuring the vapor pressure of potassium is described in detail in the corresponding references. To the author's best knowledge, the method employed in the present investigation is original, having been devised at the Liquid Metals Research Laboratory of Columbia University, by Professor C. F. Bonilla, and utilized in successively improved versions by I. L. Silver on cesium (10), V. Bhise on rubidium (11), and now by the present author on potassium. It is being scheduled to apply it shortly in its present ad-

vanced form to sodium and lithium, as well as in rechecking cesium and rubidium. As far as is known in this Laboratory, this technique has not been used before or since by any other investigator.

B. Present Physical Uses of Liquid Metals

The use of sodium to cool valves in aircraft engines has been very successful over a period of some 40 years, and is typical of the temperature level of particular interest. The Dow Chemical Company used sodium as a coolant during World War II. Steel pipe filled with sodium was used early this century as high current bus bar in electrochemical plant, and polyethylene tubing filled with sodium has served as an economical underground power cable for medium voltage distribution. Mercury boilers include vaporization and condensation phenomena; hence they are not a typical physical use for low-volatility liquid metals. A shale-oil retort employs sodium cooling of the plows that are exposed to high temperature. Baths to maintain temperature constitute another use found for liquid metals. And potassium vapor has been demonstrated by General Electric as being suitable to drive turbines for space nuclear power plants employing the Rankine cycle.

From experience with sodium and sodium-potassium alloys (NaK), it is known that steel equipment, preferably stainless, can be fabricated to contain and circulate liquid metal from room temperature up to 1400 to 1600°F. Methods of pumping, metering, heating, and cooling of the metal are available. Equipment which has been properly constructed may be cleaned, dried, filled with inert gas, and charged with sodium or NaK so as to operate for two to five years without any particular corrosion or deterioration of the liquid-metal system, provided it does not contact oxygen or moisture.

The advantages of using liquid-metals lie to a great extent in their high thermal conductivity and hence high

heat-transfer coefficients. Their stability at high temperatures and the wide range of temperatures over which they are liquids are also beneficial. These properties, plus low density (thus pumping power), high thermal conductivity and low cost have caused sodium to be selected as the primary coolant for the huge Liquid Metal Fast Breeder Reactor nuclear power program now under way.

V. CONCEPTUAL DESIGN OF THE EXPERIMENT

A. Vapor Pressure Measurements

The saturated vapor pressure of potassium was measured by utilizing the following phenomena:

At equilibrium, a homogeneous one-component (e.g., potassium), two phase system (e.g., liquid-vapor), in the absence of external forces, has only one degree of freedom. Therefore at a given temperature, the saturation, or equilibrium, vapor pressure is independent of the relative mass or volume of the liquid and vapor.

If a liquid-vapor system is not in thermal equilibrium then the resulting vapor pressure will be determined by the hottest region of the liquid.

A small bore, high pressure tube or capsule, closed at the bottom end, is attached at the open end to a S.S. tube connecting to a "Christmas Tree", and thence through high pressure valves to reservoirs, liquid injectors, a bellows and various pressure-indicating devices. The furnace tube, and somewhat higher in the system, is filled with potassium under vacuum, as schematically indicated in Fig. 5. The void space above the potassium is largely filled with liquid dodecane, which has a lower density than potassium and at the same time does not react with it, and also has a high viscosity and is available economically in good purity. The filling may be carried out so that only a relatively small void space remains, or so the system is full, but some is allowed to later escape on heating. The volume of the void is not critical as long as the S.S. tube is completely filled, and adjustments can be made.

A novel design was employed for injecting liquid into the system, to drive the potassium towards the tip of the capsule. An economical high pressure valve with a large diameter stem, to which a dial was fitted for counting turns was

used for this purpose.

During a P-T determination, the closed end of the capsule is held in the furnace at a constant temperature T . This point is intentionally the hottest location in the capsule, and the temperature gradient approaching it is kept always positive and gradual. The injection valve, which is initially opened to the maximum, is slowly closed. As the valve stem enters the valve body, this causes the liquid dodecane to push the potassium along the capsule towards the hot end, and eventually fill the capsule. In so doing, the potassium liquid/vapor interface will gradually increase in temperature, eventually reaching the temperature T at the hot end. The vapor pressure, which is the observed liquid pressure in the whole closed system, will increase accordingly, becoming equal to the saturation pressure P_{sat} corresponding to the temperature T precisely as the liquid potassium fills the capsule. Once complete filling is obtained, further valve stem insertion will result in a more rapid pressure increase due to the greater incompressibility of the potassium liquid phase than of the vapor phase. Hence, if the measured P is plotted against number of turns of the valve a curve similar to Fig. 2b results. The discontinuity in slope separating segments A and B is when the potassium just filled the tube (capsule), hence that pressure is P_{sat} associated with the tip temperature T . It has to be pointed out that only by keeping the tip as the hottest location in the capsule can one know that a measured break-point pressure is the vapor pressure corresponding to the measured tip T . If the location of the separating surface were known, it would be feasible to measure the temperature T_x at the depth H and obtain the corresponding pressure, though accuracy would not be high (Fig. 3). That is why it is necessary to force the potassium interface to the tip of the capsule slowly, when using the displacement valve. Obviously, the slope of segment

B is greater than that of segment A, due to the relative incompressibility of the liquid phase. Plots similar to Fig. 2 are obtained and from each one a single point of vapor pressure against tip temperature is obtained. Finally, this series of points is plotted as $\log P$ against $1/T$ and a graph similar to Fig. 4 is prepared. The critical point (P_c, T_c) is obtained at the break which occurs in this graph.

This pressure-measuring technique can be employed in any spacial orientation. Potassium will vaporize at the hottest location and using the injection (or displacement) valve the potassium interface is forced towards the hot tip of the small bore capsule under any circumstances. There is, however, an important advantage in operating in the "inverted" position used, with the hot tip as the lowest point in the apparatus. In this position any gas remaining in the tube during the filling operation, or evolved from the capsule walls during heating will tend to rise to the cold end of the system. In that location it cannot contribute to the observed vapor phase pressure in the capsule and introduce error into the potassium vapor pressure determination. Also, the inert gas will occupy less volume in the cold end than in the hot tip, thus "soften" the discontinuity in the P-T plot less. However, to maximize the sharpness in the plotted break, and thus the accuracy of the vapor pressure observed, all gas possible must be avoided in any location in the high pressure system.

Silver (10) noted, when using this technique for cesium, that hydrodynamic instabilities were encountered, probably due to convection currents at the hot end. However, Rhise (11) did not encounter such behavior using the same technique. In this investigation a still smaller bore was used (0.10 inch instead of 0.125 inch) and such behavior was not encountered during runs No. 3 and No. 4 with the graphite furnace.

B. Critical Point Phenomena

The critical pressure can also be obtained by this method. Assume that the tip of the capsule is at a temperature T greater than the critical temperature T_c . Thus the temperature profile of the capsule will result in T_c being located at some distance from (above, in this case) the tip.

As long as the interface has not reached the T_c location then segment A of the Pressure-Turn curve (Fig. 2b) will be a function of the surface temperature. Once the T_c location is reached, however, then two distinct phases cannot exist, and the interface disappears. The system from then on exhibits two degrees of freedom (one component, one phase) and hence ensuing pressure increases (using the displacement valve) will be a function of the equation of state for the 1-phase, taking into account its non-uniform temperature, of course. This segment B of the Pressure-Turn curve will then exhibit a slope different than the former part, but not as sharply so as below the critical point. This discontinuity will necessarily be at, and thus indicate, the critical pressure.

In order to recognize when the discontinuity in the Pressure-Turn represents P_c one must realize the following: The greatest pressure realized by segment A of the Pressure-Turn curve is P_c since this is the limit of the 2-phase-1 degree of freedom region. Thus, regardless of the longitudinal location of T_c , segment A of the Pressure-Turn curve cannot rise above P_c . Once that location is reached, segment B of the Pressure-Turn curve will exhibit

a different slope. Thus when the discontinuity occurs at the same P for various values of tip temperature T , then that $P = P_c$ and these tip temperatures are all higher than T_c . Thus, if several runs at different values of T agree on the break-point P , this must be P_c (Fig. 2b).

C. Theoretical Errors Involved

Although there are theoretical errors involved, these can be considered negligible. There will be a pressure difference across the liquid-vapor interface which is a function of the surface tension of the liquid and the radius of curvature of the meniscus; nevertheless, this pressure difference can be shown to be negligible even at room temperature in this particular case ($1/16''$ internal radius) with the capsule employed, and the difference tends to zero as the critical point is approached, due to the approach of surface tension to zero at the critical point.

There are undoubtedly molecular dimers, trimers, etc., in the vapor phase. Several experiments have sought to verify the presence of multiatoms, but this was never found (14). If any appreciable trace is present the vapor pressures of the various molecular species will be different, and an error would occur in a dynamic, or refluxing, method of obtaining pressures, where steady state evaporation and condensation are occurring. However, this particular apparatus, involving equilibrium at the interface, is free of such doubt.

VI. DESCRIPTION OF EXPERIMENTAL APPARATUS

The first apparatus used in this investigation, for runs No. 1 (11/70) and No. 2 (6/71) had been designed and utilized in the determination of the vapor pressures of rubidium and of cesium. However, some significant changes were made thereafter.

For runs No. 3(12/71) and No. 4 (3/72), a new design has made it possible to minimize the extrapolation errors, making the breaks very sharp. This is justified, as seen from the breaks obtained in runs No. 3 and No. 4 at any pressure.

A. Capsules

a) Tantalum Capsule-Bellows

The capsule employed in the experiment during runs No. 1 and No. 2 was made from a refractory alloy commercially designated T-111, which contains 90% tantalum, 8% tungsten and 2% hafnium, as a deoxidizer. This particular alloy combines high temperature strength with corrosion resistance to alkali metals and was used successfully in the cesium and rubidium work to almost comparable temperatures.

The capsule was prepared by welding three 1/2 in. O.D. rods 9 in. long which earlier had 1/8" I.D. holes drilled lengthwise through them from both ends. The intermediate ends were beveled across their full wall thickness and the sections then electric arc welded with full penetration in a vacuum chamber in the shops of the Space Power and Propulsion Section of the General Electric Company in Cincinnati. The closed tip was formed by inserting a previously machined plug of the same alloy into one end and melting it down by the electron beam method. The method devised for injecting potassium utilized a Gardner Bellows Corp. S.S. bellows of 2 in. active length and 1.002 in. O.D.

rated up to 3300 psi internally. The bellows was installed in a frame fitted with a compression screw, a turn indicator like on a micrometer gauge, and a long handle. It was able to displace a volume of 2.50 cc. when compressed approximately 0.5 in. a distance such that there was no significant decrease of bellows life due to cracking of the wall under strain or internal pressure. Unfortunately, the flexibility of the bellows, necessary for it to function as intended, also made it too compressible by the fluid. Thus, the rises in slope at the break-point were less sharp than hoped for, and this system was not adequate for accurate, high-temperature data.

b) Tungsten Capsule - Displacement Valve

The capsule employed in the experiment during runs No. 3 and No. 4 was provided by Fansteel Inc., San Fernando Laboratories, Pacoima, California. It was a Nuclear Grade Vapor-Deposited Tungsten Tube, 0.100 in. I.D. x 15 in. long x 0.3125 in. O.D. The tube was closed at one end for a length equal to the wall-thickness in the original tungsten vapor deposition process. Then, the open end was ground to exactly 0.3125 in. O.D. by centerless grinding for 2 in. in length to fit a 5/16 in. Teflon packing gland to insert into the end of the furnace, and a 5/16 in. Gyrolok fitting to connect to the potassium/oil system without leakage. This type of capsule has high temperature strength and corrosion resistance to alkali metals, but has to be handled carefully because it is brittle.

The injector, or Displacement Valve, was a high pressure, steel Hoke hydraulic valve (3514F8E), selected because of the large stem diameter and leak-resistant packing design. The valve seat was drilled out to increase the stem travel, and a volume of about 0.75 cc. could be displaced. This valve employed acylindrical, compressed Teflon packing gland. Another design (Fig. 5) had the same

stem diameter but employed a Viton O-ring seal, and was equally effective.

B. Heaters

The required high temperatures for runs No. 1 (11/70) and No. 2 (6/71) were obtained by electrical resistance heating. The resistance heater was prepared by winding 0.050 in. high purity annealed molybdenum wire on an alumina tube. The tube was 12 in. x 1-1/4 in. O.D. by 1 in. I.D. and of 99.7% purity, useable to 3540°F.

To ensure proper electrical insulation, high purity alumina powder was also applied to the alumina core. Cement was first employed to form spiral grooves on the core to guide and space the winding. Two strings of the proper thickness were wound side by side onto the core. The string simulating the wire was tied down, and the spacer string unwound. The cement was then applied, completely filling the space between the turns of the remaining string. On heating in an atmospheric furnace the cement was set and the remaining string burned away, leaving a grooved ceramic core. After the wire winding was in place and tied down at its ends, another layer of cement was spread over it, completely covering it and filling any cracks. This procedure proved entirely satisfactory. The heated tube, capsule, thermocouples, etc., were all installed in a large steel box that could stand evacuation, and was then operated filled with argon at above atmospheric pressure to protect the system against oxidation.

In this method it is indispensable that the tip of the capsule be at the highest temperature in the potassium system. Thus it was decided to wind wire along only 8 inches of the ceramic core, and the tip of the capsule was placed only slightly beyond the midpoint of the heater. Hence a good distribution of temperature was obtained.

For run No. 3 (12/71) a Centorr graphite tube furnace was used (Fig. 5), rated to 2500 C. Hence the use of the vacuum chamber and other devices (Fig. 1) was not necessary. This graphite furnace is a very important improvement because it makes the system more rigid, simpler and smaller, and saves a great deal of time in setting up a run.

Schematic diagrams of the apparatus are shown in Figs. 1 and 5.

C. Heat Shields

When the alumina tube was used as a heater in the chamber, radiation shields 0.001 inch thick of tantalum foil were used to decrease heat losses. These shields were loosely wrapped around the capsule heater. To prevent extensive contact between the foils, and hence loss of insulating value, the foils were dimpled on about one-inch centers with a dull centerpunch prior to wrapping. Approximately 10 foils were employed, held in place by 0.005 inch Molybdenum wire wrapped around the outside. The thermal insulation proved entirely satisfactory. Only 1.725 KW (81 volts at 23 amperes) were required to reach 3150°F.

When the graphite tube furnace was used some end radiation shields were added to decrease the heat losses and to make the temperature more uniform lengthwise.

D. Potassium

The potassium used in this investigation was purchased in glass capsules from the MSA Research Corporation, Callery, Pa., with a guaranteed minimum purity of 99.95% by weight. A typical analysis is given in Table 1. In view of the single phase and equilibrium nature of this method of obtaining vapor pressure and critical properties,

this purity was considered entirely adequate in an earlier study of vapor pressure by the refluxing method (33), in which the effect of all impurities by Raoult's law was considered.

E. Temperature Measurement

Tungsten-Rhenium thermocouples (W-5 Re/W-26 Re) were employed to measure the temperature of the heated tip of the capsule. The 0.010 in. diameter wire was obtained from the Hoskins Manufacturing Company of Detroit, Michigan. The calibration provided by the company every 200 F was fitted by Least Squares with a high power equation, for interpolations.

The thermocouples were first made by twisting the W-26% Rh wire around the less flexible W-5% Rh for approximately 1/4 to 1/2 inch then heliarc welding the tip into a small bead. Each hot junction thus formed was attached to the outside surface of the capsule by a loop of the 0.005 inch Mo wire. The cold junction was formed by soldering copper leads onto each individual wire and immersing them in glass tubes in an ice bath. The leads then went to a multiple-position double-pole switch that connected them to a potentiometer, a digital volt meter and also to a chart recorder.

For run No. 4 the hot junctions were not welded - instead the alternate wires were placed side by side around the end of the capsule, and the tips were tied down firmly by several turns of W-26 Re. This arrangement transferred the effective seat of the thermal EMF to the surface of the capsule from the average of the hot junction bead, undoubtedly a more accurate arrangement.

Four thermocouples were attached at the hot end of the capsule so as to increase the precision of the recorded temperature, as well as to allow for thermocouple

failures. To verify that the tip was the hottest point along the capsule, and to observe the temperature gradient directly, 2 or 3 additional thermocouples were attached at about 1/2 inch intervals away from the tip.

F. Pressure Measurement

The system pressure was read simultaneously by a transducer and a Bourdon tube test gauge. The former was of the strain gauge type, supplied by Consolidated Electrodynamics of Monrovia, California, and had a maximum range of 2500 psia. Pressure deflects a diaphragm, thus altering the electrical resistance of a strain gauge attached to it. The resulting voltage output is proportional to the applied pressure. A D.C. constant voltage power supply provided the required 10 volt input excitation. The Bourdon tube gauge was supplied by the Heise Company of Newton, Connecticut. It read directly in psig to a maximum of 3000 psig. The two devices directly gave the break pressure as the vapor pressure, except for the static head correction applied later. The arrangement of these devices is shown in Fig. 1 and 5.

The pressure transducer was calibrated in the laboratory by comparison with a dead weight gauge tester of 0.01% accuracy. The resulting calibration points were fitted to a second order polynomial by Least Squares, which was used for converting the output voltage at the break to the corresponding pressure.

G. Electrical Insulation

Electrical insulation for all thermocouples, heaters, leads, etc., was provided by inserting all components in small crushable MgO tubes, available from Norton Company for manufacture of swaged insulated thermocouples, which retain strength to some 4000 to 4200 P. In the installation for run No. 4, the principal and most effective run, unfortunately one piece of Al_2O_3 tube was placed on the wires,

near the hot junctions. This melted down at the highest temperatures and showed open circuits in two runs. However, they reestablished electrical contact and good internal agreement in later runs.

H. External Pressure System

For runs No. 1 and No. 2, an inert gas environment of the capsule heater was necessary to provide a non-reacting atmosphere for Ta, Mo, W and Re components. High purity Airco argon (99.997%) was employed. The hot end of the capsule and the capsule heater were placed in a 1 x 2 x 4 foot vacuum chamber (provided by Brookhaven National Laboratory). To preclude air leakage into the chamber, an argon pressure of 5 psig was employed. A vacuum pump was employed for outgassing the chamber initially, at the lower temperatures, then flushing out oxidizing gases before adding the argon.

In runs No. 1 and No. 2, where the chamber was used with a positive pressure of argon, an additional heater containing Getterloy (Zr-Ti) turnings which is an alloy that removes oxygen when heated, was installed so the argon would circulate slowly through it by thermal convection. It was heated to about 800°F, as indicated by sheathed thermocouples, for a period of 6 days before a run.

For runs No. 3 and No. 4 in which the graphite furnace replaced the chamber, the system was more compact and easier to operate (Fig. 5). Some 4 psig of argon was maintained during the runs, plus a small continuous bleed-off, to prevent in-leakage of air.

I. Power System

1. Runs No. 1 and No. 2

Electrical power to heat the capsule was single phase at 208 volts, fed through a variable autotransformer.

To prevent possible damage in case of an electrical grounding of the heater, the entire system, including the vacuum chamber, gas cylinder, etc., was insulated from the ground. In addition, quick-acting fuses were installed in the line. These fuses, obtained from Chase Shauman Manufacturing Company of New York, are known commercially as "Amp. Trap". They are designed to blow when the rated amperage is exceeded by 1% for one cycle. For each new power setting, the next higher rating fuse was inserted into the line.

2. Run No. 3 and No. 4

In these runs, the graphite furnace was directly used. This graphite furnace is a very good improvement because all devices (voltmeter, ammeter, wattmeter, etc.) are integrated in one unit. This makes it very useful and easy to operate.

J. Recording Instruments

The thermocouples and pressure transducer outputs were read simultaneously on a Leeds and Northrup portable precision potentiometer and a Weston digital voltmeter of 4-1/2 digits and 100 mV full-range. Thus the resolution of the instrument is 10 microvolts. An 8-point recorder with a full scale reading of 5 mV recorded the outputs of the tip thermocouples and the pressure transducer. Since the outputs from these sources were in general greater than 5 mV it was necessary to buck them before recording. An arrangement was made so that each bucking voltage, as well as each individual output, could be measured directly on the potentiometer and the digital voltmeter.

Since for any one P-T measurement the tip temperature is maintained constant, the recorder was used to monitor small changes ($\Delta 2^{\circ}\text{F}$) in the tip temperature. A switch

permitted any one of the tip thermocouples to be recorded at one time. During any run the recorded input was switched continually between the thermocouples to note any possible fluctuations or discrepancies in thermoelectric output.

During a P-T run the pressure in the system continuously varies, and consequently the pressure transducer output will vary proportionally. All pressure changes could be observed directly on the recorder with reasonable sensitivity. A number of the sharper breaks in the Pressure-Turn curves were directly visible on the recorder.

K. Miscellaneous

Lead for the thermocouple wires and the power leads and the capsule into the vacuum chamber and the graphite furnace came through Conax glands with drilled Teflon bushings.

Gyrolok fittings were used to join all tubing, including the vital Ta-111 to 316 S.S. joint. These fittings provided excellent seals.

Heating tape was wrapped around all tubing and fittings outside of the vacuum chamber or the graphite furnace which contained potassium, to keep the potassium molten.

The optical pyrometer was a model of the Leeds and Northrup Company.

VII. EXPERIMENTAL PROCEDURE

A. Charging the Capsule

The capsule was charged with potassium by a simple method (Fig. 8). The desired mass of potassium (10 grams) was ordered from MSA Research in a glass ampule with a tip which could be easily broken off. The ampule is attached to the system by Silicone tubing. The system is evacuated through (2) and then argon is run in from (4) to a positive gage pressure. This process is repeated several times to be sure that any trace of air is removed from the system. The ampule and tube are then left under pressure, closed off with a clamp, disconnected from the system, and the tip broken off inside the tube. Applying a second clamp nearer the ampule and opening the first, the tip and all chips are removed. Then the ampule is attached to the apparatus again, the system evacuated again and the ampule, capsule, and intermediate tubing warmed to about 400 F. The potassium is liquified and flows into the capsule.

To avoid using a large volume of potassium, and decrease corrosion problems and the possibility of potassium solidifying in a cold region, it was decided to employ an inert liquid to finish filling the system. It was decided to use chemically pure n-dodecane, $C_{12}H_{26}$. It is a saturated aliphatic hydrocarbon, thus non-reactive with alkali metals as well as with the materials of construction. It has a lower density (thus will not mix with the potassium), reasonably high boiling point (thus will not vaporize at reasonably low pressures, at and substantially above the melting temperature of potassium), and a reasonably high viscosity (to decrease leakage rate through piping joints when under high pressures, which would impair the sharpness of the breaks in slope). It also has some compressibility (which is somewhat undesirable, but unavoidable) and has an appreciable thermal expansion

(a factor needed by Silver (10) and Ehise (11) in their experiments, but not by the present method). Obviously the $C_{12}H_{26}$ can only be employed above the potassium, so when the capsule was used in the inverted position, as at present, to facilitate rising of any gas trapped or evolved, the capsule and the approach tube where the interface was established were straight

B. Wetting Behavior Test

Wetting tests were made several times after charging the S.S. tube-tungsten capsule system with potassium to check the wetting behavior of potassium and the location of the oil-potassium interface. Locating this interface accurately (Fig. 9) is possible due to the difference in the electrical resistance between dodecane and potassium if the potassium has wetted to S.S. wall. Wetting of the tube wall also seems to be necessary to prevent the oil also used in the system from penetrating and carbonizing below the top level of the potassium, specially if the potassium is allowed to freeze. Once one knows where the interface is, it is possible to keep checking its position frequently, to verify that no leakage, reaction or decomposition is taking place.

The d-c circuit devised to keep constant current flowing along the tubes (Fig. 9), was mounted vertically. The voltage drop, which was then proportional to the resistance, was measured continuously with a Digital Voltmeter.

Equipment Used:

- 1) Digital Voltmeter (Weston Model 1294)
- 2) Three-Volt Battery
- 3) 0-30 Ampere Ammeter
- 4) 9 Ohm Rheostat

As an illustration, the results of one of these tests are shown in Fig. 10.

C. Preliminary Operations

Prior to runs No. 1 and No. 2 the vacuum chamber was evacuated and degassed. Then it was flushed twice with argon, and finally maintained at 5 psig (at room temperature) to preclude in-leakage of air.

For runs No. 3 and No. 4 the graphite tube furnace was used. The furnace was purged by flowing pure argon gas through it at 20 CFM for about ten minutes or by evacuating it with a mechanical pump and back-filling it with argon several times. After initial purging, the gas flow was reduced to 2 to 3 CFH, while still maintaining a slightly positive pressure. Details of the graphite tube furnace are in reference (12).

Prior to charging, the capsule was degassed at 800°F overnight under vacuum.

D. Procedure for Obtaining Data

For preliminary estimates of the saturation pressure, the vapor pressure curve determined by Bowles (7) was extrapolated, since it reached the highest previous temperatures. Prior to a P-T determination, while a steady tip temperature was being reached, the displacement valve was adjusted so that the pressure was approximately 100 psi below the estimated vapor pressure. The bucking potentials were adjusted so that the outputs of the pressure transducer and the tip thermocouples were bucked to within about 0.5 mV. This meant that these quantities were all printed out starting near the left hand edge of the chart of a Leeds and Northrup recorder of 5 mV full scale.

Before beginning a run all the corresponding data were read, such as power, A.C. Amperes, A.C. Volts, optical pyrometer temperature, and the thermocouple EMFs at the tip of the capsule. It was first made sure that the temperature at the tip was steady. Then, the pressure in the system

was increased by slightly turning the displacement valve. The Heise Bourdon Tube gage was read visually, an assistant calling out the observed reading. Carrying out a series of observations at fairly regular intervals, the break in each plot of pressure vs. time was very sharp and clearly visible on the recorder chart. This was assisted by the excellent distribution of temperature along the graphite heater tube in the furnace.

Four thermocouples were used at the tip of the capsule. The thermocouples were continually switched so that any discrepancy developing in one of the thermocouple outputs would soon be noticed.

Three of the four tip thermocouples regularly showed a temperature about 4°F lower than the fourth one. It was decided to use the average temperature indicated by the three lower-reading thermocouples because the thermocouples which made the best contact with the capsule would naturally read lower than any which might be slightly loose.

For each run, the pressure in the system was increased slowly by hand using the displacement valve so that each pressure observation took about 3 minutes. This time interval was found to be entirely adequate to reach a steady pressure reading after a normal increment of about 1/10 turn of the valve handle.

Although a number of the pressure breaks were visible directly on the pressure-time recorder graphs of the pressure transducers, the Heise readings were plotted against angle of the valve stem to yield the more accurate "official" plots. The breaks in these curves, as obtained with a straight edge or French curve, provided the accepted P_{sat} at each tip temperature.

These graphs are given in Appendix I.

VIII. EXPERIMENTAL RESULTS

The experimental data consist of the pairs of equilibrium break-pressure vs. tip-temperature points, and are listed in Table II. The Heise gage has a guaranteed maximum error of any reading of 0.1% of full scale (3 psi). Also, for each pressure-displacement plot there is an extrapolation error in determining P_{sat} . Allowing an apparent maximum error of 1 psi here, the probable maximum error in each P_{sat} is

$$\sqrt{3^2 + 1^2} = 3.16 \text{ psi}$$

If this corresponds to about 3%, the error is about 1 psi.

The transducer had been calibrated independently against a deadweight tester and its output fitted to a parabola, $E = a + bP + cP^2$, where E is in mV and P is in psia. The value of "a" was not constant due to fluctuations of the excitation voltage. Since such behavior is not normal, according to the manufacturers, the transducer indications of P_{sat} were not employed in fixing each P_{sat} , except as a mean of checking the location of the breaks in the curves with respect to the Heise gauge observations.

The tip thermocouples could be read to an accuracy of ± 0.02 mV. This corresponds roughly to a maximum reading error of 2°F in tip temperature.

IX. VAPOR PRESSURE RELATIONS

A. General Considerations

The phase rule states that the vapor pressure of a pure liquid is a single-valued function of the saturation temperature. Almost all vapor-pressure data are thus expressed in a form

$$P = f(T)$$

P could be related to any other intensive property of the saturated liquid or vapor, but the temperature is most convenient.

All vapor-pressure equations may be traced back to the Clapeyron equation,

$$\begin{aligned} dP/dT &= \Delta H_v / T \Delta V_v = \Delta H_v / (RT^2/P) \Delta Z_v \\ \text{or} \quad d(\ln P)/d(1/T) &= -\Delta H_v / R \Delta Z_v \end{aligned} \quad (a)$$

Equation (a) is easily derived from thermodynamics by using the phase equilibrium criteria, that the fugacities (or chemical potential), temperatures, and pressures are equal in both phases. The key to the integration of Equation (a) is the evaluation of the ratio $\Delta H_v / \Delta Z_v$. As a first approximation it is often assumed constant, Equation (a) leading to Young's equation,

$$\ln P = A + B/T \quad (b)$$

Allowing $\Delta H_v / \Delta Z_v$ to vary linearly with temperature leads to Kirchoff's equation,

$$\ln P = A + B/T + c \ln T \quad (c)$$

These relations have been widely used in correlating experimental vapor pressure data.

Although most authors agree that above a reduced temperature of about 0.85 there is a distinct curvature, as evidenced by the use of the $\ln T$ term in equation (c), a plot of $\ln P$ against $1/T$, due to its near-linearity is, however, a very helpful way to present and study vapor-pressure data (46).

A typical curvature of actual $\ln P$ vs. $1/T$ is illustrated (and exaggerated) in Fig. 10-A. Thodos (40) and Waring (42) studied this curvature for many materials and found that the point of inflection in Fig. 10-A occurs in or near the range $T_r = 0.8$ to 0.85.

The plot of the new raw potassium data in Fig. 11, after allowing for the natural scatter, evidently exhibits some curvature.

B. Semi-Empirical Equations for the Vapor Pressure of Liquids as a Function of Temperature

Numerous other equations, both empirical and theoretical, have been given relating vapor pressure P with absolute temperature T . Many published integrations of Equation (a) are based on more complex empirical rules for the variation of ΔH_v and ΔZ_v with temperature. The most common more advanced relation is due to Frost and Kalkwarf (43), who assumed that (1) the heat of vaporization is a linear function of temperature,

$$\Delta H_v = \Delta H_{ro} + \Delta C_s T \quad (d)$$

(2) van der Waals' equation satisfactorily represents the volumetric behavior of the gas, and (3) the molal volume of the liquid is approximated by the van der Waals' constant b . The general form of the equation derived is,

$$\ln P = A + B/T + C \ln T + D P/T^2 \quad (e)$$

Equation (e) is not well suited for hand calculations, as it cannot be solved explicitly for pressure, but is easily handled by a high-speed computer.

Miller (41), in a search for accurate vapor pressure correlations more suitable to hand computation, chose an equation explicit in pressure,

$$\ln P = A + B/T + C T + D T^2 \quad (f)$$

Equation (f) written in terms of the critical point is relatively easy to use.

C. Relations Investigated

An extended set of relations suitable for correlating vapor pressure were investigated to determine the one giving the statistical best fit with these data,

- (1) $\ln P = a + b/T + c \ln T$
- (2) $\ln P = a + b/T + c \ln T + d/T^2$
- (3) $\ln P = a + b/T + c \ln T + d P/T^2$
- (4) $\ln P = a + b/T + C T^m \quad -2 \leq m \leq 3$
- (5) $\ln P = a + b/T + C T + d T^2$

There exists no general method for finding the best type of formula to fit any given set of data. A good procedure is to consider the following points:

- (1) The standard deviation
- (2) Resemblance of the curve generated in the range under consideration
- (3) Extrapolated results
- (4) The curve of error.

It is important to plot the data on rectangular coordinate paper, taking care to choose the proper scales along the two axes so as to make the degree of fit show up clearly.

In this investigation the curve of error was considered to be very important in comparing the equations.

The following correlations were obtained on curve-fitting the data in terms of $\ln P$. In all cases P is in psia, T in $^{\circ}R$, and the standard deviation, σ , is of $\ln P$.

$$(1) \quad \ln P = 5.80348 - \frac{1.44182 \times 10^4}{T} + 0.661435 \ln T$$

$$\sigma = 0.0123358$$

$$(2) \quad \ln P = 1.77218 - \frac{7.6242 \times 10^3}{T} + 1.01101 \ln T - \frac{9.2435 \times 10^6}{T^2}$$

$$\sigma = 0.00494329$$

$$(3) \quad \ln P = 0.189237 - \frac{1.53218 \times 10^4}{T} + 1.43296 \ln T \\ - \frac{4.24293 \times 10^3}{T^2}$$

$$\sigma = 0.00493668$$

The standard deviation shown by Equation (3) is seen to be very slightly lower than that of Equation (2), with the same number of coefficients. Thus Equation (3) is the most representative of the data. However, in view of the very small difference in the σ 's and the much greater convenience of an equation which is explicit for P, equation (2) would be preferable in most cases.

Setting $P_c = 2380.00$ psia, an average value from the four experimental observations, Equation (3) yields,

$$T_c = 4101.89^\circ \text{R}.$$

X. CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The design of the experiment described in this report is well suited to the measurement of high temperature vapor pressures. In addition, it provides an excellent means of determining the critical pressure and temperature of a liquid.

By forcing the liquid under investigation to fill the capsule one requires a minimal active volume, compared to all other methods. This reduces corrosion and containment problems, also requiring only a single local, and hence a more definite and more accurately determinable temperature. Also, this method provides its own high pressures not requiring an external high pressure system, simplifying the equipment needs. These are distinct advantages when one considers the material compatibility problems facing high temperature experimenters.

It is desirable to determine the critical constants of the other alkali metals, sodium and lithium, and this method having been successful with cesium, rubidium and potassium, seems the most convenient so far developed. A more detailed investigation of the liquid region near the critical point would give a better understanding of the nature of metallic inter-molecular bonding and thus provide clearer utilization of the law of corresponding states.

After finishing runs No. 1 and No. 2, in which the T-111 was used, the bore of the capsule was found to be plugged. The same happened to Rhise (11) while working on rubidium using the same T-111 capsule. It is believed that oil crept down and was carbonized in the hot region of the tube.

For run No. 3, in which a tungsten capsule was used the same problem occurred, the capsule plugging up several inches from the open end. On due consideration it was realized that in all of the earlier runs on Cs, Rb and K the alkali metal had been allowed to freeze in the capsule between runs, presumably from the open end towards the tip, since the open end would lose heat more rapidly as well as never reaching as high a temperature. It was thus concluded that the shrinkage on freezing had allowed oil to penetrate, possibly all or almost all of the way to the tip. On the next heat-up this oil would have cracked, which evidently plugged the tube.

Following this theory, the potassium was kept above its freezing point throughout the 4th series of runs and in between, and no plugging was observed. In addition, it was allowed to freeze away from the tip, by turning off the furnace first, then gradually cutting down the heat from the heating tapes along the rest of the potassium-filled tube.

It is expected that this shut-down process will avoid all plugging, and allow the same K-filled capsule to be used for added check runs if desired, without cleaning out and later recharging.

It was noted that the two supercritical runs (Figs. 49 and 55) for which the tip temperatures were determined as 4347.2 and 4264.2 °R showed an increase in slope at P_c , in the same direction as the subcritical runs. On the other hand, the two supercritical runs (Figs. 48 and 50) for which the tip thermocouples were inoperative showed a decrease in slope at P_c . For these two runs furnace power was also not recorded, so it is not evident that their tip temperatures exceeded those of Figs. 49 and 55, but it seems likely they did. Though the direction of this change in slope was roughly verified theoretically from the known properties of water, its principal significance is probably only the practical one that future supercritical runs by this method should be carried out in small increments of tip temperature above T_c , as in some particular temperature range no break in slope would be observed. Also, the sharpness of the break might be expected to be greater the smaller the supercritical volume in the capsule, although this is not actually indicated by the available Figs. 47 and 55. Literature data on Al_2O_3 temperatures also do not clarify what happened, as the melting point is quoted at 4058 to 4150°R and the boiling point at an improbably low 4408°R in handbooks. Thus all four runs must have had tip temperatures above the melting point of alumina. Also, it is difficult to visualize that boiling of the alumina could have occurred, or been involved, if it did, in the change in slope at P_c .

XI. APPENDIX I

Representative Experimental Data

The Heise gauge readings were all plotted to give the Pressure-Turn curves. These curves are included here for all points. None of the supercritical points (14,15,16, 17,22) were used in the curve-fit analysis. Points 20 and 24 were also eliminated, due to being slightly off the curve. The values of the Heise gauge pressure shown in the graphs include the static head correction. The corrected data are presented in Table II.

XII. APPENDIX II

A. Calibration of Pressure Transducer

The pressure transducer was calibrated against a deadweight tester which had an accuracy of 0.1%. The data from this calibration were fitted with a parabola by least squares, yielding:

0 - 2500 psia transducer

$$E = 4.42371 + 0.0161497 P - 8.74115 \times 10^{-9} P^2$$

(P in psia and E in mV)

B. Calibration of the Tip Thermocouples

The calibration points supplied by the manufacturer (Hoskins Manufacturing Company of Detroit, Michigan) for each 200 F increment were used. A cubic least squares fit gave:

$$E = -3.49752 + 1.34026 \times 10^{-2} T - 8.29845 \times 10^{-7} T^2$$

$$- 1.47126 \times 10^{-11} T^3$$

(T in °F and E in mV)

TABLE IAnalysis of Potassium Used*

<u>Element</u>	<u>Analysis, ppm by weight</u>
Fe	< 5
B	< 10
Co	< 5
Mn	1
Al	< 2
Mg	2
Sn	< 5
Cu	< 1
Pb	< 5
Cr	< 5
Si	25
Ti	< 5
Ni	< 5
Mo	< 3
V	< 1
Be	< 1
Ag	< 1
Zr	< 10
Sr	< 1
Ba	< 3
Ca	8
Na	15
K	balance

* High purity grade in glass capsules, from MSA Research Inc.

TABLE IIExperimental Data(Heise Gauge Readings after Calibration
and Static Head Corrections)

<u>Run and Date</u>	<u>Point No.</u>	<u>Temperature (°R)</u>	<u>Vapor Pressure (psia)</u>
#3(12/71)	1	2559.09	203.40 **
	2	2732.79	311.77
	3	2934.94	477.70
	4	3093.79	644.20
	5	3248.99	831.50
	6	3374.14	1007.20
#4(3/72)	1	2727.69	309.20
	2	3073.14	625.80
	3	3221.69	800.07
	4	3389.94	1032.34
	5	3521.44	1229.60
	6	3667.49	1488.24
	7	3850.69	1843.20
	8	3820.79	1776.15
	9	2940.69	483.74
	10	3387.39	1026.70
	11	3721.69	1600.40
	12	4026.69	2228.00
	13	4058.19	2264.00
	14	4134.99	2341.00
	15		2377.00 *
	16	4347.19	2381.00 *
	17		2382.00 *
	18	2790.69	356.24
	19	3370.44	996.30
	20	3299.09	880.00 **
	21	4033.49	2206.00
	22	4264.09	2380.00 *
	23	3818.44	1766.05
	24	4058.19	2211.00 **

* Supercritical points not included in the curve-fit.

** Other points not included in the curve-fit due to
larger deviations from smooth curve (See Fig. 11).

Semi-Empirical Equations for the Vapor Pressure of Potassium
as a Function of Temperature

$$(1) \ln P = 5.80348 - \frac{1.44182 \times 10^4}{T} + 0.661435 \ln T$$

Std. Deviation of $\ln P = 0.0123358$
 (T in $^{\circ}\text{R}$, P in psia)

$$(2) \ln P = 1.77218 - \frac{7.6242 \times 10^3}{T} + 1.01101 \ln T - \frac{9.2435 \times 10^6}{T^2}$$

Std. Deviation of $\ln P = 0.00494329$
 (T in $^{\circ}\text{R}$, P in psia)

$$(3) \ln P = 0.189237 - \frac{1.53218 \times 10^4}{T} + 1.43296 \ln T - \frac{4.24293 \times 10^3}{T^2} P$$

Std. Deviation of $\ln P = 0.00493668$
 (T in $^{\circ}\text{R}$, P in psia)

TABLE IIIComparison of Curve-Fit Results

Point No.	Temperature (R)	Observed Pressure (psia)	Equation(1) (psia)	Equation(2) (psia)	Equation(3) (psia)
Run#3					
1	2559.09	203.40 **	212.51	203.30	203.30
2	2732.79	311.77	317.82	312.54	312.38
3	2934.94	477.70	479.18	479.95	479.97
4	3093.79	644.20	638.53	644.20	644.27
5	3248.99	831.50	824.00	832.96	833.36
6	3374.14	1007.20	996.02	1006.26	1006.62
Run#4					
1	2727.69	309.20	314.31	308.90	308.74
2	3073.14	625.80	616.11	621.03	621.25
3	3221.69	800.07	789.17	797.65	798.03
4	3389.94	1032.34	1019.21	1029.47	1029.82
5	3521.44	1229.60	1225.10	1234.24	1234.39
6	3667.49	1488.24	1481.35	1485.79	1485.58
7	3850.69	1843.20	1844.54	1836.70	1836.10
8	3820.79	1776.15	1782.07	1776.78	1776.22
9	2940.69	483.74	484.43	485.38	485.41
10	3387.39	1026.70	1015.44	1025.70	1026.05
11	3721.69	1600.40	1583.93	1585.54	1585.19
12	4026.69	2228.00	2237.71	2210.01	2209.57
13	4058.19	2264.00	2312.66	2280.48	2280.17
14	4134.99	2341.00			
15		2377.00 *			
16	4347.19	2381.00 *			
17		2382.00 *			
18	2790.69	356.24	359.53	355.90	355.76
19	3370.44	996.30	990.65	1000.86	1001.23
20	3299.09	880.00 **	889.86	899.55	900.40
21	4033.49	2206.00	2253.77	2225.13	2224.71
22	4264.09	2380.00 *			
23	3818.44	1766.05	1777.21	1772.11	1771.55
24	4058.19	2211.00 **			

* Supercritical points not included in the curve-fit.

** Other points not included in the curve-fit due to larger deviations from smooth curve (see Fig. 11).

TABLE IV

Best Estimate of the Vapor Pressure of Potassium
from this Investigation

Equation(3)

<u>Temperature</u> <u>°F</u>	<u>Vapor Pressure</u> <u>psia</u>	<u>Temperature</u> <u>°F</u>	<u>Vapor Pressure</u> <u>psia</u>
2000	154.69	2410	420.89
2010	158.98	2420	429.63
2020	163.58	2430	438.48
2030	168.27	2440	447.45
2040	173.05	2450	456.53
2050	178.07	2460	465.72
2060	182.90	2470	475.03
2070	187.97	2480	484.46
2080	193.13	2490	493.99
2090	198.38	2500	503.65
2100	203.74	2510	513.41
2110	209.21	2520	523.29
2120	214.74	2530	533.29
2130	220.39	2540	543.41
2140	226.13	2550	553.64
2150	231.98	2560	563.98
2160	237.93	2570	574.44
2170	243.98	2580	585.02
2180	250.13	2590	595.71
2190	256.38	2600	606.52
2200	262.74	2610	617.45
2210	269.20	2620	628.50
2220	275.76	2630	639.66
2230	282.43	2640	650.94
2240	289.20	2650	662.33
2250	296.08	2660	673.85
2260	303.07	2670	685.48
2270	310.16	2680	697.23
2280	317.36	2690	709.10
2290	324.67	2700	721.08
2300	332.08	2710	733.18
2310	339.60	2720	745.41
2320	347.24	2730	757.75
2330	354.98	2740	770.20
2340	362.83	2750	782.78
2350	370.79	2760	795.47
2360	378.86	2770	808.29
2370	387.04	2780	821.22
2380	395.33	2790	834.27
2390	403.74	2800	847.44
2400	412.26	2810	860.73

TABLE IV(Continued)

<u>Temperature °F</u>	<u>Vapor Pressure psia</u>	<u>Temperature °F</u>	<u>Vapor Pressure psia</u>
2820	873.13	3310	1676.27
2830	887.66	3320	1695.59
2840	901.30	3330	1715.02
2850	915.07	3340	1734.58
2860	928.95	3350	1754.24
2870	942.95	3360	1774.02
2880	957.07	3370	1793.93
2890	971.30	3380	1813.94
2900	985.66	3390	1834.07
2910	1000.14	3400	1854.32
2920	1014.73	3410	1874.68
2930	1029.45	3420	1895.16
2940	1044.28	3430	1915.76
2950	1059.23	3440	1936.47
2960	1074.30	3450	1957.30
2970	1089.49	3460	1978.25
2980	1104.79	3470	1999.30
2990	1120.22	3480	2020.48
3000	1135.76	3490	2041.77
3010	1151.43	3500	2063.17
3020	1167.21	3510	2084.70
3030	1183.11	3520	2106.33
3040	1199.13	3530	2128.08
3050	1215.27	3540	2149.95
3060	1231.52	3550	2171.93
3070	1247.90	3560	2194.02
3080	1264.39	3570	2216.23
3090	1281.00	3580	2238.56
3100	1297.73	3590	2260.99
3110	1314.58	3600	2283.55
3120	1331.55	3610	2306.22
3130	1348.63	3620	2329.00
3140	1365.83	3630	2351.90
3150	1383.15	3640	2374.90
3160	1400.59		
3170	1418.15		
3180	1435.82	3642.20(Tc)	2380.00(Pc) *
3190	1453.61		
3200	1471.52		
3210	1489.55		
3220	1507.69		
3230	1525.96		
3240	1544.34		
3250	1562.83		
3260	1581.45		
3270	1600.18		
3280	1619.03		
3290	1637.99		
3300	1657.08		

* Critical Point

Fig. 1. Experimental Set Up with the Vacuum Chamber.

Conceptual Behavior of Potassium Vapor Pressure as a Function of Turns of Displacement Valve for Various Capsule Tip Temperatures.

Fig. 2a. Typical behavior when capsule temperature is less than the critical temperature.

Fig. 2b. Typical behavior when capsule temperature is greater than the critical temperature.

Fig. 3. Distribution of Temperature Throughout the Capsule.

Fig. 4. Vapor Pressure Vs Temperature Up to the Critical Point.

Fig. 5. Experimental Set Up with the Graphite Furnace.

Capsule-Heater Power System (Used with the vacuum chamber)

Heating Tape Power System

Fig. 6. Electrical Power System.

Thermocouple Output Recording System

Transducer Output Recording System

Fig. 7. Recording System.

Fig. 8. Set Up for Charging the Capsule.

Fig. 9. D.C. Circuit for Tests of Wetting Behavior of Potassium.

Fig. 10. Test of Wetting Behavior for Locating the Interface (Oil-Potassium).

Fig. 10-A. Schematic Vapor-Pressure Plot(exaggerated).

RUN No. 1(11/70)

The data obtained in this run "are not reliable" due to the inability to get good breaks in the pressure curves. The lack of definite breaks is probably caused by evaporation and carbonization of dodecane getting into the capsule alongside the wall and reaching a position where the temperature was high enough to effect this problem. The points taken around the break off pressure (which are the most important, of course) were obtained with certain uncertainty while the system pressure was jumping and giving signals of the instability of the system. However, the set is presented here as an illustration.

The measured tip temperatures and the vapor pressures expected are given. These values of vapor pressures are obtained from Equation (2), which is based on a fit of the data of runs NO.3 and No.4.

Fig. 12

Tip Temperature: 2200.47°R

Vapor Pressure Expected:
52.27 psig.

Fig. 15

Tip Temperature: 3248.52°R

Vapor Pressure Expected:
817.50 psig

RUN No. 2

(6/71)

Data "not reliable" for the same causes of run No.1

Fig. 22

Tip Temperature: 2312.38°R

Vapor Pressure Expected:

82.60 psig

RUN No. 3

(12/71)

Data gotten up to:

3374.19°R

1007.20 psia

Fig. 28

Tip Temperature 2559.69°R

Measured Vap. Pressure:
203.40 psia

— Heise Gauge Pressure (psia) —

300

250

200

150

0

— Turns of Displacement Valve —

1

2

3

4

5

Fig. 30
Tip Temperature: 2934.69°R
Measured Vap. Pressure:
477.70 psia

Fig. 31
Tip Temperature: 3093.69°R
Measured Vap. Pressure:
644.20 psia

Fig. 33

Tip Temperature: 3374.19°R

Measured Vap. Pressure:
1007.20 psia

— Heise Gauge Pressure (psia) —

1050

1000

950

0

1

2

— Turns of Displacement Valve —

RUN No. 4

(3/72)

Data gotten up to:

3900°~~F~~(4360°R)

2380 psia *

* 2380 psia is the " Critical Pressure " obtained by
four supercritical points.

The " Critical Temperature " was indirectly determined
by the best-fit equation.

CRITICAL PRESSURE: 2380.00 psia

CRITICAL TEMPERATURE: 4101.89°R

Fig. 34

Tip Temperature: 2727.69°R

Measured Vap. Pressure:
309.20 psia

Fig. 36

Tip Temperature: 3221.69°R

Measured Vap. Pressure:
800.07 psia

Fig. 42

Tip Temperature: 2940.69°R

Measured Vap. Pressure:
483.74 psia

Fig. 43

Tip Temperature: 3387.19°R

Measured Vap. Pressure:

1026.70 psia

XIII. ADDENDUM

The critical point of potassium had not been determined by any other investigator before due to the lack of any other good method, and of any other serious program to achieve it.

Dillon (23) extrapolated his potassium density data and predicted a critical temperature of 4001°R and a critical pressure of 2351 psia.

This novel method for measuring vapor pressure of liquid metals has been designed and developed successfully in the Liquid Metals Research Laboratory, Columbia University, New York, 1972. With the equipment components at the present level of development, the method was shown to be very reproducible, as can be observed from run No. 3 (12/71) and run No. 4 (3/72).

XIV. NOMENCLATURE

A,B,C,	Regression coefficients in vapor pressure equation.
ΔC_s	Difference between heat capacities of saturated vapor and liquid.
E	EMF in millivolts of thermocouples or transducer.
m	Exponent of T^m term.
n	Number of data points.
P	Pressure, psia.
P_c	Critical pressure, psia.
P_{sat}	Vapor pressure (at break-point of P-turns plot).
R	Gas constant
T	Capsule tip temperature (equilibrium temperature in °R in equations).
T_c	Critical temperature.
T_r	Reduced temperature, T/T_c
H_v	Latent heat of vaporization, per unit mass.
H_{vo}	Constant in Equation (d).
ΔV	Volume change per unit mass on vaporization.
Z_g, Z_l	Compressibility factor for saturated vapor; saturated liquid.
ΔZ_v	Equal to $Z_g - Z_l$

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