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**CRITICAL TEMPERATURES AND DENSITIES
OF THE ALKALI METALS**

by

**Ira G. Dillon, P. A. Nelson,
and B. S. Swanson**

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

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Chemical Engineering Division

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IN NUCLEAR SCIENCE ABSTRACTS

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NOMENCLATURE

A = atomic weight
 A_c = activity at counter, cpm
 A_s = activity at source, cpm
 b = proportionality constant
 b = constant in Rydberg function = $2\pi\nu[A/2D_c]^{1/2}$
 B = second virial coefficient
 B_A = attractive potential function
 B_R = repulsive potential function
 c = constant
 C = third virial coefficient
 D = fourth virial coefficient
 D_e = minimum of depth of potential energy function at $r = r_e$
 f = self-shielding factor
 k = Boltzmann constant
 k = reduction of activity due to other factors than attenuation
 M = slope of vapor pressure curve at the critical point = $\frac{d \ln P}{d \ln T} = \alpha$
 M = molecular weight, g/g-mole
 MW = molecular weight, g/g-mole
 n = neutrons
 n = number of moles
 N_0 = Avagadro's number = 6.023×10^{23} atoms/g-atom
 P = pressure, atm
 P_c = critical pressure, atm
 P_r = reduced pressure P/P_c
 R = gas constant
 r = distance between nuclei
 r = radius of cylinder, cm
 r_e = equilibrium distance between nuclei
 T = temperature ($^{\circ}K = t + 273.16$)
 T_c = critical temperature, $^{\circ}K$
 $T_r = T_{red}$ = reduced temperature T/T_c
 t = temperature, $^{\circ}C$
 t = time, min
 V = volume, liters

$\tilde{V}$ = molar volume, liters/g-mole
 V_c = critical volume, liters/g-mole
 V_r = reduced volume $\tilde{V}/V_c$
 X = atomic fraction of material
 Z = compressibility factor $P\tilde{V}/RT$
 Z_c = critical compressibility factor $P_c V_c / RT_c$
 γ = gamma
 ΔH_v = heat of vaporization, cal/g-mole
 α = slope of vapor pressure curve at the critical point = $M = \frac{d \ln P}{d \ln T}$
 ϵ = potential energy at minimum distance between nuclei
 θ = interaction temperature, $^{\circ}K$
 λ = decay constant, min^{-1}
 μ = gamma-ray absorption coefficient, cm^2/g
 ν = frequency of vibration
 ξ = shielding factor $\mu r \rho$
 ω = eccentric factor = $-\log P_r - 1.0$
 ρ = distance from minimum potential = $r - r_e$
 ρ = density, g/cc
 ρ_c = critical density, g/cc
 ρ_L = liquid density, g/cc
 ρ_v = vapor density, g/cc
 σ = distance between nuclei at zero potential energy

Subscripts

c refers to critical point
 e refers to potential
 o reference number
 r refers to reduced property
 s refers to source
 L refers to liquid phase
 v refers to vapor phase
 v refers to vaporization
 A refers to attractive function
 R refers to repulsive function

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SUMMARY

Vapor and liquid densities of the alkali metals sodium, potassium, rubidium, and cesium were measured from room temperature to near the critical points by a method which utilized radioactive isotopes of the alkali metals. The critical temperature and critical density were then estimated by extrapolation to the critical point.

For these density measurements, a metal capsule of tungsten or Mo-30% W was charged with a calculated amount of alkali metal. The capsule was sealed and irradiated in a thermal-neutron flux to obtain radioactive isotopes of the alkali metal being tested. The capsule was subsequently placed in a heated assembly made of Mo-30% W which was insulated by tungsten carbide powder contained in a silicon carbide crucible. Gamma radiation emanating from the vapor and liquid regions in the capsule passed through the thin (30 mil) capsule wall and telescoping holes in the work piece to a sodium iodide crystal outside the furnace. The measured radiation was proportional to the density of the vapor or liquid.

The critical temperature and critical density were obtained by several methods of correlation. These included the rectilinear diameter plots of Cailletet and Mathias,²² correlations developed by Rowlinson⁵⁸ and by Kordes,⁶⁷ and a generalized correlation of reduced density with reduced temperatures. Critical temperatures of the alkali metals estimated by these correlating methods were as follows: for sodium, $2573 \pm 350^\circ\text{K}$; for potassium, $2223 \pm 330^\circ\text{K}$; for rubidium, $2093 \pm 35^\circ\text{K}$; for cesium, $2057 \pm 40^\circ\text{K}$. The respective critical densities were 0.206 ± 0.041 , 0.194 ± 0.037 , 0.346 ± 0.009 , and 0.428 ± 0.012 g/cc. These values fall between predictions of Grosse⁹ and data of Hochman and Bonilla^{56,57} for cesium and rubidium. Based on data obtained in this work for other alkali metals and liquid-density data for lithium of Tepper *et al.*,⁸⁵ the estimated critical temperature for lithium is $3223 \pm 600^\circ\text{K}$ and the estimated critical density 0.120 ± 0.033 g/cc.

Heats of vaporization for the alkali metals as a function of reduced temperature were calculated by means of the Clapeyron equation

from the vapor and liquid densities of this work, and the vapor pressure equations of Sawhney and Bonilla.¹⁴

This study has shown that the alkali metals deviate somewhat from the "law of corresponding states" based on nonmetallic substances. Also, the behavior of alkali metals has been shown to be somewhat different from that of mercury in that the shape of the density vs. temperature curves is different and the entropy of vaporization is lower than that of mercury at reduced temperatures above 0.5.

The method of measurement employed could also be used in many cases to determine vapor and liquid densities at high temperatures for metals, alloys, fused salts, and other materials.

CHAPTER 1

INTRODUCTION

Importance of Problem

The purpose of this investigation was to obtain an understanding of the behavior of the alkali metals in the region of the critical temperature. The properties of rubidium, cesium, sodium, and potassium were investigated experimentally, and those of lithium were calculated from the data obtained from the other metals by a corresponding-state technique. Lithium was not investigated experimentally because its critical pressure and temperature are beyond the limits of materials of construction presently available and because it does not have a suitable radioactive isotope.

Critical constants have both a fundamental and applied significance. From the standpoint of physical chemistry, the data give insight into the nature of liquid metals as evidenced by their nonideal behavior. From the chemical engineering point of view, the data give a basis for prediction of many other physical properties of these alkali metals over a wide range of conditions as well as information to use in forming a basis for prediction of behavior of other metals.

The advent of nuclear power resulted in a concentrated research effort in the alkali metal field. Many of the physical and chemical properties of alkali metals make them attractive for use as reactor coolants. These include low neutron cross section, short half-life of the radioactive isotopes produced by neutron bombardment, good heat transfer characteristics, and low corrosiveness. Sodium and NaK have been extensively investigated for the last 15 years; lithium has also been investigated in connection with the Aircraft Nuclear Propulsion program. Potassium has

been investigated in connection with SNAP and SPUR space programs. The need for ion engine fuels and turbine fluids in space applications is rapidly expanding the use of rubidium and cesium. Several programs for investigating the properties of these materials are currently being carried out and will be mentioned in the next section.

Review of the Literature

For the metals, actual measurements of critical temperature exist only for mercury. Early attempts to measure the critical temperature of mercury were made by Traubeau and Teichner,^{1*} by Koenigsberger,² by Menzies,³ and by Bender.^{4,5} Bender⁵ also reported the density of liquid mercury and its saturated vapor. The Chemical Engineer's Handbook⁵⁵ gives low-temperature data for the density of liquid mercury (see Table 1). The vapor pressure of mercury has been measured by several investigators, including Cailletet *et al.*⁶ and Bernhardt.⁷ Low-pressure data (below 1 atm) and medium-pressure (up to 12 atm) data have been reported in the Chemical Engineer's Handbook.⁵³ Calculations were made for the entire range by Epstein and Powers.⁵⁴ These data

TABLE 1. Density Data for Mercury^{5,55}

Saturated Vapor		Liquid	
Temp, °C	Density of Saturated Vapor, g/cc	Temp, °C	Density of Liquid, g/cc
1050	0.70	0	13.60
1210	1.15	100	13.35
1230	1.35	200	13.11
1295	1.65	300	12.88
1330	1.90	350	12.74
1380	2.50	500	12.38
1460	4.70	600	12.10
		800	11.60
		900	11.15
		1000	10.55
		1100	10.00
		1200	8.85
		1300	8.25
		1460	4.70

*For all numbered references, see bibliography.

are shown in Table 2 and plotted in Fig. 1. The only investigator to measure the critical temperature (1733°K) and the critical pressure (1587 ± 50 atm) of mercury was Birch.⁸

TABLE 2. Vapor Pressure Data for Mercury^{53,54}

Temp, °C	Pressure, mm Hg	Pressure, atm
126.2	1	0.0013
164.8	5	0.0066
184.0	10	0.013
204.6	20	0.026
228.8	40	0.053
242.0	60	0.079
261.7	100	0.132
290.7	200	0.263
323.0	400	0.526
357.0	760	1.000
360.0	808	1.063
375	1,034	1.36
399	1,550	2.04
418	2,067	2.72
433	2,584	3.40
449	3,101	4.08
458	3,618	4.76
468	4,134	5.44
501	6,202	8.16
515	7,235	9.52
527	8,269	10.88
538	8,542	12.24
550	10,762	14.16
600	17,571	23.12
650	27,436	36.10
700	40,219	52.92
750	57,274	75.36
800	78,964	103.9
850	111,264	146.4
900	138,852	182.7
950	178,296	234.6
1,000	220,932	290.7
1,050	279,832	368.2
1,100	343,672	452.2
1,150	417,620	549.5
1,200	502,892	661.7
1,250	601,084	790.9
1,300	714,096	939.6
1,350	844,360	1,111
1,400	994,080	1,308
1,450	1,168,120	1,537
1,460 (critical temperature)	1,206,120	1,587 (critical pressure)

Fig. 1. Vapor Pressure of Mercury^{53,54}

Recently an attempt was made by Hochman and Bonilla to measure the critical temperature and density of cesium and rubidium by an electrical resistance method.^{30,56,57,69,83} Extrapolation of their conductivity data gave critical-temperature estimates of 2100°K for rubidium and of 1996°K for cesium.

Estimates of the critical temperatures of metals have been made by Grosse,⁹⁻¹² Zadmukin,¹³ and others.^{33,52} Measurements of the vapor pressure of alkali metals have been made by Bonilla *et al.*,^{14,31} Bowles and Rosenblum,¹⁵

Kirillov and Grachev,¹⁶ Cochran,¹⁸ Gray,¹⁹ Young and Deutsch,²⁹ and Sowa.⁸⁴ Vapor pressures of alkali metals are given in Table 3 and plotted in Fig. 2. Density data (experimental or calculated) for the alkali metals have been reported by Sittig⁴⁵ (sodium only), in the Liquid Metals Handbook,⁴⁶ by Weatherford, Tyler, and Ku,^{47,62} by Meisl and Shapiro,¹⁷ by Achener,⁶⁰ by Tepper *et al.*,⁶¹ and by Stone *et al.*^{65,71} Liquid and vapor density are given in Table 4.

TABLE 3. Vapor Pressures of Rubidium, Cesium, Sodium, and Potassium^{14,31}

Absolute Pressure, atm	Temperature, °C			
	Na	K	Cs	Rb
0.02	(566.10)	(452.74)	383.29	(402.17)
0.05	623.46	(506.27)	433.12	452.44
0.1	672.33	522.31	476.15	495.71
0.2	726.85	604.14	524.76	544.48
0.3	761.75	637.59	556.23	576.00
0.5	809.36	683.54	599.60	619.33
1.0	881.42	753.86	666.25	685.73
1.5	928.20	800.00	710.19	729.36
2.0	963.76	835.34	743.94	762.76
2.5	992.83	864.39	771.75	790.32
3.0	1017.61	889.28	795.63	813.92
4.0	1058.76	930.85	835.62	853.35
5.0	1092.52	965.21	868.76	888.96
6.0	1121.40	994.76	897.33	914.05
7.0	1146.80	1020.88	922.64	938.88
8.0	(1169.55)	(1044.38)	945.47	961.24
10.0	(1209.25)	(1085.63)	(985.62)	(1000.52)
15.0	(1287.27)	(1167.59)	(1065.77)	(1078.68)
180	-	-	-	(1917) ^a
190	-	-	(1877) ^a	-
240	-	(2167) ^a	-	-
490	(2507) ^a	-	-	-

^aCritical Temperature (estimated by Grosse⁹).

Fig. 2
Vapor Pressure of
Cesium, Rubidium,
Potassium, and
Sodium^{14, 31}

TABLE 4. Density Data for Sodium, Potassium, Cesium, and Rubidium^{47,60,61,62,65,71}

Sodium ^{47,62,65}			Potassium ^{47,62,71}		
Temp, °C	Density of Saturated Liquid, g/cc	Density of Saturated Vapor, g/cc	Temp, °C	Density of Saturated Liquid, g/cc	Density of Saturated Vapor, g/cc
97.9 (mp)	0.970	-	63.5 (mp)	0.860	-
115.6	0.930	4.0×10^{-13}	115.6	0.822	1.0×10^{-10}
171.1	0.913	2.0×10^{-12}	171.1	0.806	2.4×10^{-9}
226.7	0.897	4.2×10^{-10}	226.7	0.790	2.7×10^{-8}
282.2	0.882	4.7×10^{-9}	282.2	0.775	1.9×10^{-7}
337.8	0.866	3.3×10^{-8}	337.8	0.760	9.2×10^{-7}
393.3	0.852	1.7×10^{-7}	393.3	0.746	3.4×10^{-6}
448.9	0.838	6.7×10^{-7}	448.9	0.732	1.0×10^{-5}
504.4	0.824	2.2×10^{-6}	504.4	0.719	2.6×10^{-5}
560.0	0.811	6.0×10^{-6}	592.0	0.703	-
615.6	0.798	1.4×10^{-5}	671.1	0.682	0.0002
671.1	0.786	3.1×10^{-5}	850.0	0.643	-
726.7	0.774	6.1×10^{-5}	955.0	0.617	-
782.2	0.762	1.1×10^{-4}	1052.0	0.590	-
858.2	0.752	0.0004	1161.0	0.562	-
1023.0	0.709	0.0008	1253.0	0.541	-
1145.3	0.678	0.0017	855.6	-	0.00108
1242.7	0.655	0.0027	969.8	-	0.00226
1366.2	0.628	0.0046	1030.8	-	0.00314
			1093.2	-	0.00433
			1199.6	-	0.00676
			1304.1	-	0.01018

TABLE 4. (Contd.)

Cesium ^{47,60,62}			Rubidium ^{47,61,62}		
Temp, °C	Density of Saturated Liquid, ⁶⁰ g/cc	Density of Saturated Vapor, ^{47,62} g/cc	Temp, °C	Density of Saturated Liquid, ⁶¹ g/cc	Density of Saturated Vapor, ^{47,62} g/cc
28.4 (mp)	1.900	-	39.0 (mp)	1.530	-
267.8	1.727	-	69.9	1.477	-
412.2	1.647	-	204.6	1.440	-
547.2	1.564	-	313.4	1.385	-
694.4	1.495	-	442.2	1.319	-
738.6	1.435	-	513.3	1.294	-
763.8	1.426	-	590.0	1.264	-
832.8	1.388	-	656.1	1.235	-
910.2	1.333	-	722.5	1.200	-
1004.4	1.284	-	827.6	1.148	-
1060.0	1.250	-	892.9	1.118	-
1115.6	1.211	-	952.2	1.087	-
115.6	-	9.7×10^{-9}	1058.8	1.034	-
226.7	-	9.7×10^{-7}	1090.0	1.028	-
337.8	-	1.8×10^{-5}	337.8	-	7.3×10^{-6}
448.9	-	1.3×10^{-4}	448.9	-	6.3×10^{-5}
560.0	-	5.4×10^{-4}	560.0	-	0.0003
615.6	-	0.0016	671.1	-	0.0010
782.2	-	0.0038	782.2	-	0.0025
893.3	-	0.0075	893.3	-	0.0053
1004.4	-	0.0131	1004.4	-	0.0098
1115.6	-	0.0208	1115.6	-	0.0160
1226.7	-	0.0308	1226.7	-	0.0250

Estimates of the critical constants of the alkali metals have been made by Grosse.⁹ His estimates are shown in Table 5.

TABLE 5. Estimates of the Critical Constants of Alkali Metals⁹

Metal	MW	P _C , atm ^a	T _C , °K ^b	ρ _C , g/cc	V _C , liters g-mole	Z _C ^c
Na	22.990	490	2780	0.18	0.128	0.275
K	39.102	240	2440	0.18	0.217	0.260
Cs	132.905	180	2150	0.42	0.316	0.322
Rb	85.47	190	2190	0.32	0.267	0.282

^aP_C = ±10%.

^bT_C = ±300°K.

^cCalculated from Grosse's estimates.

Grosse⁹ has developed methods of correlating data based on the "law of corresponding states" originally proposed by Van der Waals²⁰ for gases and extended to liquids by Young.²¹ This law states that at corresponding reduced conditions ($T/T_C = T_R$; $P/P_C = P_R$; $D/D_C = D_R$; etc.) all gases have the same properties. This law was further modified by Hougen *et al.*^{24,26} to include the correlating variable $Z_C = P_C V_C / RT_C$, where Z_C is the critical compressibility factor, P_C the critical pressure,

V_c the critical volume, T_c the critical temperature, and R the gas constant. Lydersen *et al.*^{27,75} developed an independent correlation of the critical compressibility factor by relating it to the molal heat of vaporization as follows:

$$Z_c = \frac{1}{3.43 + 0.0067(\Delta H_v)_b},$$

where $(\Delta H_v)_b$ is the heat of vaporization at the normal boiling point (in kcal/g-mole). Reid^{26,75,76} introduced the slope α of the vapor pressure curve at the critical temperature as a third parameter:

$$\alpha = \frac{d \ln P}{d \ln T} \text{ (at the critical point).}$$

A related parameter ω , called the acentric factor because it measures the deviation of the intermolecular potential function from that of spherical molecules, was selected by Pitzer *et al.*⁷⁷ in terms of reduced saturation pressure at a reduced temperature of 0.70 by the relation

$$\omega = -\log P_r - 1.0.$$

Curl and Pitzer^{26,78} reported that more reliable correlation could be obtained by the use of the ω parameter than by the use of Z_c because of the uncertainty in estimation of critical density when evaluating Z_c . If experimental data for critical density are not available, more accurate values of Z_c can be calculated from values of α or ω as follows:

$$Z_c = \frac{1}{1.28\omega + 3.41} = \frac{1}{0.26\alpha + 1.90}.$$

Grosse⁹ has correlated many properties of cesium and rubidium based on estimated values of critical temperature and critical density. Since his report⁹ was published, density and vapor pressure data have become available for sodium, potassium, rubidium, and cesium up to a temperature of 2700°R. These data may be used together with Grosse's methods of plotting to verify his estimates of critical density. For example, he plots the one-half reduced density (gas density plus liquid density/two times the critical density) of rubidium and cesium from the melting point to the estimated critical point. A linear relationship is assumed, that is, the law of rectilinear diameters (law of Cailletet and Mathias). If the experimental data^{47,60,61,62,65,71} are plotted as reduced temperature vs. reduced density, assuming the critical density values estimated by Grosse, the rectilinear-diameter lines are straight for sodium, potassium, cesium, and rubidium. Also, the reduced liquid density curve is very close to the ideal liquid curve plotted by Grosse based on the equations of Guggenheim:²³

$$\rho_L/\rho_C = 1 + 3/4(1 - T_r) + 7/4(1 - T_r)^{1/3}; \quad (1)$$

$$\rho_V/\rho_C = 1 + 3/4(1 - T_r) - 7/4(1 - T_r)^{1/3}; \quad (2)$$

$$\frac{\text{Rectilinear Diameter}}{\text{Diameter}} = \frac{\rho_L + \rho_V}{2\rho_C} = 1 + 3/4(1 - T_r). \quad (3)$$

The rectilinear-diameter lines may then be replotted as one-half reduced density vs. temperature (in °K). For mercury, other important relationships are plotted by Grosse. He correlates $\Delta H_{\text{vap}}/T$ vs. T_{red} ; if one could assume that alkali metals would behave similarly, this curve would be used to predict critical temperatures of alkali metals.

Theory

The "law of corresponding states" was first proposed by Van der Waals²⁰ and extended to liquids by Young.²¹ The basic assumptions behind this principle, five in number, have been outlined by Guggenheim:²³

1. use of classical statistical mechanics (quantum effects must be negligible);
2. spherically symmetrical molecules, either actually or by virtue of rapid and free rotation;
3. intramolecular vibrations the same in the liquid and gas states;
4. the potential energy taken as a function only of the various intermolecular distances (as Mayer³⁷⁻³⁹ has pointed out, this is consistent with the properties of saturated molecules where the only attractive forces are of the Van der Waals-London type);
5. the potential energy for a pair of molecules can be written $\Phi(r)$, where r is the intermolecular distance and Φ is a uni-

versal function. A typical plot of this function is given by Pitzer³⁶ and is shown in Fig. 3.

Fig. 3. Characteristic Potential Energy Function³⁶

The application of the "law of corresponding states" to metals has been examined by Pitzer.³⁶ Pitzer defines a "perfect" liquid as one which obeys all five assumptions. Metal properties were found to differ considerably from those predicted for a "perfect" liquid. The entropies of vaporization of metals are less than predicted. The decrease of heat capacity with vaporization is also less

than predicted, but is about the same for most metals. Metals melt at temperatures much less than predicted in some cases less than one-half that predicted for a "perfect" material. The coefficient of expansion for metals is considerably smaller than for chemically saturated substances.

Among the metals, even lithium is essentially unaffected by quantum considerations, and it seems likely that lack of spherical symmetry can be an important consideration. On the other hand, the possibility of thermal excitation of electronic motion may be important. Also, metallic binding forces are quite different from the Van der Waals-London forces of the saturated molecules. Pauling⁴⁰ and others^{41,42} have discussed theories of metallic binding. The assumption that the potential energy can be expressed in terms of intermolecular forces alone is no longer valid. Assumption (5) would not be expected to hold for alkali metals, since both attractive and repulsive forces exist.

Insofar as the five assumptions are fulfilled, the following equation of state is valid for gas, liquid, and solid:

$$\frac{P}{P_c} = u\left(\frac{T}{T_c}, \frac{V}{V_c}\right), \quad (4)$$

where u is a universal, but complicated, function. Equation (4) can be written in the form

$$Z = f\left(\frac{P}{P_c}, \frac{T}{T_c}\right) = f(P_{\text{red}}, T_{\text{red}}) = f(P_r, T_r), \quad (5)$$

where Z is the compressibility factor ($PV = ZnRT$). Based on the principle that all gases have the same compressibility factors when measured at the same reduced conditions of pressure and temperature, generalized charts have been developed^{24,25} for derived properties such as fugacities, and for departures from ideal-gas behavior of enthalpy, entropy, and heat capacity. Watson²⁶ extended these generalized charts to the liquid state. According to Equation (2), the critical compressibility factor Z_c should be the same for all substances; Watson found that these values actually ranged from 0.20 to 0.30 for the materials tested. If one uses values of V_c , P_c , T_c estimated by Grosse,⁹ one calculates that for mercury, $Z_c = 0.48$, but for the alkali metals Z_c is in the range 0.20 to 0.30. With this modification the "theorem of corresponding states" becomes

$$Z = f(P_r, T_r, Z_c). \quad (6)$$

Correlations with Z_c as the third parameter have been made by Lydersen et al.²⁷ and by Meissner and Seferian.²⁸

Another approach to estimation of physical and thermodynamic properties of gases is the use of an equation of state employing "virial" coefficients. A common form is the following:

$$\frac{P\tilde{V}}{RT} = 1 + \frac{B}{\tilde{V}} + \frac{C}{\tilde{V}^2} + \frac{D}{\tilde{V}^3} + \dots; \quad (7)$$

the constants B, C, and D are called the second, third, and fourth virial coefficients, respectively.

For engineering purposes "at sufficiently low pressures" well below the critical point ($P_r < 0.5$), a satisfactory estimate of thermodynamic properties can usually be made using just the second virial coefficient. Equation (7) then becomes

$$\frac{P\tilde{V}}{RT} = 1 + \frac{B}{\tilde{V}} \quad (8)$$

The system is then defined if the second virial coefficient is determined. Thorn and Winslow⁴⁹ have suggested the following equation (based on the work of Sinanoğlu and Pitzer⁸¹) for the second virial coefficient for potassium (which should also be valid for the other alkali metals):

$$B = 1/4 B_A + 3/4 B_R. \quad (9)$$

Here B_A is the attractive potential function and B_R the repulsive potential function. According to Thorn and Winslow, these functions are given by

$$B_A = 2N_0 \int_0^\infty \{1 - \exp[-\Phi_A(r)/kT]\} r^2 dr; \quad (10)$$

$$B_R = 2N_0 \int_0^\infty \{1 - \exp[-\Phi_R(r)/kT]\} r^2 dr, \quad (11)$$

where N_0 is Avogadro's number, k the Boltzmann constant, r the distance between nuclei, and T the temperature (in °K). Selection of the potential function Φ_A was made according to the suggestion of Varshni.⁵⁰ For Φ_A the Rydberg function is chosen

$$\Phi_A = -D_e(1 + b\rho) \exp(-b\rho), \quad (12)$$

where $\rho = r - r_e$, with r_e the value of r at the minimum of depth, D_e as given in Fig. 3, and b a constant. The repulsive function Φ_R is given by the following equation:

$$\Phi_R = D_e \left(1 + b\rho + \frac{b}{\rho} \right) \exp(-b\rho) \text{ for } \rho > 0, \quad (13)$$

where

$$b = 2\pi\nu(A/2D_e)^{1/2}$$

ν the frequency of vibration, and A the atomic weight.

Walling and Lemmon⁵¹ have given data for the molecular constants of dimers of the alkali metals and mercury. These are given in Table 6.

TABLE 6. Molecular Constants for the Ground Electronic States of Alkali Metals and Mercury Dimers⁵¹

Substance	D_e/k , °K	D_e , ergs	ν , cm^{-1}	r_e , Å	b
Na ₂	8590	1.185×10^{-12}	159.23	3.078	3.72
K ₂	6030	0.832×10^{-12}	92.64	3.923	4.27
Rb ₂	5690	0.785×10^{-12}	57.28	4.13	4.24
Cs ₂	5230	0.722×10^{-12}	41.99	4.47	4.38
Hg ₂	700	0.097×10^{-12}	36	3.3	9.3

Walling and Lemmon used this approach to scale the vapor pressure measurements on Na, Rb, Cs, and Hg to the vapor pressure curve for potassium. Predictions of the scale factors were made from parameters of the Rydberg attractive potential function and triple point constants. Triple point constants were used since critical constants were not known for alkali metals. Over the limited temperature range (570-1200°C) of their correlation, the alkali metals appeared to have the same reduced vapor pressure at any given reduced temperature, but this did not hold too well for mercury over this temperature range.

CHAPTER II

DESCRIPTION OF APPARATUS

Densities of the vapor and liquid phases of alkali metals were determined by a method in which the gamma activities emanating from known isotopes of alkali metals (see Table 7) produced by thermal-neutron irradiation of the pure metal were counted. The critical temperature and critical density were obtained from appropriate plots of the density data which ranged from room temperature to the critical value.

TABLE 7. Radioactive Isotopes Used in Determining
Critical Constants of Alkali Metals

Isotope	Half-life	Gamma Energy, MeV	Precursor (n, γ Reaction)	Abundance of Precursor, % ^a	Thermal-neutron Cross Section, b
Rb ⁸⁶	18.7 d	1.08	Rb ⁸⁵	72.5	1
Cs ¹³⁴	2.1 yr	0.605	Cs ¹³³	100	28
K ⁴²	12.5 hr	1.53	K ⁴¹	6.88	1.1
Na ²⁴	15.0 hr	2.75	Na ²³	100	0.53

^aAbundance prior to irradiation of capsule in thermal-neutron flux.

Measurement of quantities at these high temperatures (up to 2200°K) and high pressures (up to 500 atm) requires special materials and techniques. Since at elevated temperatures metals oxidize and react readily, it is necessary to have a very pure atmosphere. This can be accomplished by having either a very pure inert atmosphere or by operating under high vacuum. The latter technique was used in these studies, since it was desirable to remove continually gas released by the insulation.

A 30-in.-diameter by 5-ft-high vacuum tank was used as the containment vessel. A combination of a Stokes Microvac roughing pump and a diffusion pump maintained a vacuum of about 1μ absolute pressure. In order to obtain the high temperatures required, the cylindrical workpiece was insulated with powdered tungsten carbide contained in a ceramic crucible. The alkali metal itself was contained in a thin-walled capsule which, in turn, was contained in a massive refractory metal cylinder to provide both shielding from radiation and support against the high-pressure forces developed within the capsule when the capsule and its contents were heated. The massive refractory metal cylinder (workpiece) had two stepped-diameter holes (simulating tapered holes which reduce scatter of radiation) leading from the vapor- and liquid-phase regions of the capsule wall toward the outside of the vacuum tank to the single-channel analyzer which counted the collimated gamma-radiation beams from the alkali metal.

The alkali metal was contained in a molybdenum-30 w/o tungsten, molybdenum-98 w/o tungsten, or pure molybdenum capsule, $1\frac{1}{2}$ in. long

and 1/4 in. in OD (see Fig. 4). This material of construction was chosen because data^{34,35,43,44,47,59} indicated that molybdenum and tungsten have

108-7293

Fig. 4. Capsule for Containment of Alkali Metals

side a tantalum can by guide pins. The center piece was drilled radially to hold the capsule. The capsule was held in place by threaded end plugs.

excellent corrosion resistance to alkali metals. The capsules were charged by means of the assembly shown in Fig. 5. Prior to being charged, the alkali metals were contained in glass ampoules sealed under inert gas or vacuum. Charging was carried out in a high-purity helium-atmosphere glovebox. The capsule was charged with a weighed amount of material from the ampoule, evacuated, and then sealed under vacuum by deforming the molybdenum gasket by driving the tapered plug down with the pressed rod (see Fig. 5). The sealed capsule was then removed from the capsule charging assembly and welded as shown in Fig. 4.

The capsule was contained in a cylindrical block of molybdenum-30 w/o tungsten. The original design (see Figs. 6 and 7) of the block called for a 2-in.-diameter by 6-in.-long cylinder in 3 pieces, held in a fixed position inside a tantalum can by guide pins. The center piece was drilled radially to hold the capsule. The capsule was held in place by threaded end plugs.

Fig. 5

Capsule-charging Assembly

108-7969

108-7950 Rev.

Fig. 6. Original Design of High-temperature Cell Block for Determination of the Critical Temperature of Alkali Metals

108-7968 Rev.

Fig. 7. Overall Furnace Assembly for Original Design of Apparatus for Determination of the Critical Temperature of Alkali Metals

Since these plugs tended to seize under the extreme pressures and temperatures of the experiments, an improved design involving a 2-part split workpiece was constructed (see Fig. 8). This included a tapered molybdenum-30 w/o tungsten block of slightly over 2-in. diameter held in place by a 3-in.-diameter sleeve. This afforded more strength and easier removal of the capsule after heating. The workpiece was contained in a 30-mil-thick tantalum can to prevent reaction of the insulation with the molybdenum-tungsten block. The assembly was insulated by 6- μ -diameter tungsten carbide powder inside a silicon carbide crucible.

Fig. 8

Revised Furnace Assembly for Critical Temperature Apparatus

1. Insulation	7. Mo-30 w/o W Capsule Containing Alkali Metal in 3/16-in. ID Narrow Section 1-in. Long by 30-mil Wall
2. 1/4-in. Tantalum Tubes Connecting to Temperature Measurement Holes in Tapered Mo-30 w/o W Cylinder	8. Locating Pin
3. Fiberfrax Lid	9. Silicon Carbide Crucible (6 1/2-in. OD x 11 in. high x 1/2-in. Wall)
4. Tantalum Can and Lid	10. 1/4-in. Tantalum Tubes Connecting to Collimation Holes in Mo-30 w/o W Cylinder
5. Tapered Mo-30 w/o W Cylinder in 3-in. OD Mo-30 w/o W Sleeve	11. 1/2-in. "Veeco" Fittings in Wall of Vacuum Tank
6. Locating Pin	12. Refractory Supports

108-8548

Silicon carbide crucibles were chosen after testing alumina, magnesia, and zirconia crucibles, all of which tended to crack and disintegrate with very little use. Ceramically bonded alpha-silicon carbide has a high thermal conductivity plus a low coefficient of thermal expansion and high strength, all of which contribute to excellent thermal shock resistance.⁶⁴ These SiC crucibles have shown no apparent change in strength or appearance after many (20-50) thermal cycles of the workpiece from room temperature to 2000°K (crucible temperature reached 1500°K maximum). The original crucible dimensions were 5 3/4-in.-OD by 9 3/4 in. high by 7/16-in. wall; for the improved design, dimensions were 6 1/2-in.-OD by 11 in. high by 1/2-in. wall. A crucible lid made of Fiberfrax held the powder in place. The crucible was supported by a Lava stand which was adjustable in the vertical dimension. As shown in Fig. 8, beam holes and thermocouple

holes extending through the workpieces were connected to 1/4-in. tantalum tubing which extended out through the top and bottom of the crucible. The two 1/4-in.-diameter tantalum tubes extending from the beam holes lined up with the two "Veeco" fittings in the wall of the vacuum tank.

The counting equipment outside the vacuum tank consisted of a single-channel analyzer and associated equipment. This equipment included two high-voltage sources, two preamplifiers, a scaler, two 1-by-1-in. NaI thallium-activated crystals packaged with photomultiplier tubes, and a recorder.

Selection of the Material of Construction of the Capsule

An important consideration in this work was the corrosion of the materials of construction. Originally, both the high-pressure cell and the capsules were made of molybdenum-30 w/o tungsten alloy. This alloy failed at a temperature of about 1750°C when containing rubidium, at 1675°C when containing cesium, and at 1950°C when containing sodium. Originally it was planned to obtain density data for mercury, but it was not possible to contain this material at any reasonable temperature.

The alloy, 98 w/o tungsten-2 w/o molybdenum was tried. It was not successful in containing mercury, but was found to be a better container material for cesium and rubidium.

Another problem was encountered with potassium, which required the maximum possible irradiation. This activated the tungsten in the molybdenum-30 w/o tungsten container (capsule) material to such an extent that the sample was too radioactive to handle in the facilities available at the site of the experiment. This problem was solved by the use of two other container materials: pure molybdenum and TZM alloy (0.5 w/o titanium, 0.08 w/o zirconium, balance molybdenum), whose use reduced the container activity to a level such that it could be handled.

Selection of Gasket Material for Sealing the Capsules

The original choice for the gasket for forming the original capsule seal prior to welding was tantalum, which could be readily deformed by the press rod in the capsule-charging assembly. From Fig. 6 one can see that the gasket is located well above the top beam hole. Even though it was known that the tantalum gasket would become radioactive, it was thought that the resultant gamma energy would be sufficiently degraded by the time it passed through the molybdenum-30 w/o tungsten shielding that it would not interfere with counting. However, the degraded radiation was of such great intensity and energy that it obscured all other spectra in energy ranges below 1 MeV. Therefore, a different gasket material had to be found.

Three criteria for selection quickly limited the available materials:

1. Vickers hardness number less than 350;
2. resistance to alkali metal corrosion at 3500°F;
3. no high-energy (>0.5 -MeV) gamma produced by neutron irradiation.

Application of these criteria limited the choice of materials to annealed molybdenum and annealed rhenium. Tests of annealed rhenium showed that it was too hard and did not deform properly. Consequently, annealed molybdenum was chosen as the gasket material, and it performed quite well.

CHAPTER III

EXPERIMENTAL PROCEDURES

Calibration of Thermocouples

The thermocouples used were of tungsten-5% rhenium/tungsten-26% rhenium. These were calibrated by use of a Model 8622-C Leeds and

108-7970

Fig. 9. Comparison of Tungsten-5% Rhenium/Tungsten-26% Rhenium Thermocouple Readings with Optical Pyrometer Readings

Northrup Optical Pyrometer, itself calibrated with a standard tungsten lamp filament and against a standardized pyrometer. The maximum error, in comparison with the other pyrometer and the tungsten lamp, was less than 10°C. The pyrometer was then used to check the calibration of thermocouples over the temperature range 700 to 1900°C. A typical calibration curve is shown in Fig. 9. A standard procedure in obtaining the data was to calibrate thermocouples before and after a run to be certain there was no "drift" in thermocouple voltage with repeated temperature cycling.

Irradiation of Molybdenum-Tungsten Alloy to Determine the Background Correction for Counting

Alkali metals were activated for counting by first sealing them in a molybdenum-30 w/o tungsten capsule (see Fig. 4) and irradiating the sealed capsule with a thermal-neutron flux. It was desirable to know the contribution of the irradiation container material (molybdenum-30 w/o tungsten) to the total activity from the capsule as a function of time. Consequently, a 1-in.-long by 1/2-in.-OD molybdenum-30 w/o tungsten cylinder was irradiated in the CP-5 reactor for 14 days at a flux of 10^{12} n/(cm²)(sec). The data in Fig. 10 show that 30-day cooling would be required to reduce the activity to a point to where it would make essentially no contribution to a counter located 15 in. from the source.

The shape of the curve in Fig. 10 indicates that the activity is due primarily to two isotopes: tungsten-187 having a half-life of 24 hr and molybdenum-99 having a half-life of 66 hr. However, if one is counting isotopes with higher gamma energies than those of tungsten-187 (0.8 MeV)

or molybdenum-99 (0.74 MeV), then the activity from these two isotopes can be eliminated by setting the window level of the single-channel analyzer to count only the desired energy. Therefore, no container decay time is necessary for sodium-24 (2.75-MeV gamma energy and 15-hr half-life) or potassium-42 (1.75-MeV gamma energy and 12.5-hr half-life). Another correction to counting discussed in Appendix A is the effect of self-shielding.

Fig. 10. Gamma Irradiation from a Molybdenum-30 w/o Tungsten Cylinder, of 0.5-in. OD, and 1.0 in. Long, Irradiated 14 days at $10^{12} \text{ n}/(\text{cm}^2)(\text{sec})$

Calibration of Counting Equipment

The counting equipment described in Chapter II was calibrated by use of the following standards:

<u>Element</u>	<u>Form of Standard</u>
Cesium	Cesium nitrate salt
Rubidium	Rubidium metal
Potassium	Potassium nitrate salt
Sodium	Sodium nitrate salt

These were irradiated in the CP-5 research reactor so as to give a counting rate of about 50,000 cpm. These were all counted with the single-channel analyzer, giving expected counting rates and spectra that agreed well with those reported by Crouthamel.⁶³

Operating Procedure

The 12 basic steps in making a run were as follows:

- (1) Charge material to the capsule.
- (2) Test the capsule for integrity by heating to 1275°C.
- (3) Irradiate the charged capsule in CP-5.
- (4) Cool the capsule for the necessary length of time.
- (5) Charge the capsule to the workpiece.
- (6) Charge the workpiece to the furnace assembly.
- (7) Evacuate the vacuum tank.
- (8) Heat the furnace assembly to a predetermined steady-state temperature.
- (9) Record temperatures; record the gamma radiation from the vapor and liquid phases of the alkali metal by counting with the single-channel analyzer.
- (10) Adjust induction-heating controls to obtain a new higher steady-state temperature and then repeat step (9).
- (11) Cool the furnace to room temperature.
- (12) Remove the furnace assembly from the vacuum tank for disassembly and recharging.

Charging the capsule involved the use of (1) a high-purity inert atmosphere (helium containing ≤ 10 ppm total $H_2O + O_2$) glovebox and

(2) the capsule-charging assembly shown in Fig. 5. The desired amount of alkali metal was charged to the capsule body by means of a one-cc hypodermic syringe for cesium (which melts at 28°C) and a scalpel for rubidium, sodium, and potassium (which are solids at room temperature). The amount of material charged was determined by weighing on an Ainsworth analytical balance contained within the glovebox. After the alkali metal (or mercury) was charged to the capsule body, the capsule body, gasket, and plug (see Fig. 4) were placed in the capsule-charging assembly and the capsule was sealed under a vacuum of 20 μ . Final closure was made by Heliarc welding of the capsule.

The capsule was tested for integrity by heating to 1275°C in the inductively heated furnace assembly contained in the vacuum tank. The capsule was reweighed after heating to ascertain if any alkali metal had escaped.

If the capsule were found to be sound, it was irradiated in the CP-5 research reactor to a calculated level of activity. Irradiations can be made in this reactor at thermal-neutron fluxes up to $5 \times 10^{13} \text{ n}/(\text{cm}^2)(\text{sec})$. In order to obtain a reading of about 100,000 cpm at the counter, outside the vacuum tank which contained the furnace assembly, it was necessary to irradiate the alkali metal to a level of about 50 mCi of activity (2×10^9 disintegrations per second).

After the irradiated capsule was removed from the reactor, it was cooled for about 20 days in the case of cesium (2.1-yr half-life) and rubidium (18.7-d half-life) to permit decay of the 1-d W^{187} and the 2.75-d Mo^{99} produced by irradiation of the Mo-30 w/o W capsules containing the alkali metals. Much shorter cooling times were required for sodium (15-hr half-life) and potassium (12.5-hr half-life). Sodium and potassium could be run after 1-day cooling of the capsule because the high-energy gamma activities ($>1.5 \text{ MeV}$) could be counted without interference from W^{187} (0.7 MeV) and Mo^{99} (0.74 MeV).

When the capsule was sufficiently cooled, it was charged to the workpiece. In early work this was the three-section design shown in Fig. 6. When the capsule was placed inside this workpiece, the radiation level at the surface of the workpiece was reduced by a factor of ten from the activity measured at the surface of the capsule. When the capsule was placed inside the split-design workpiece (see Fig. 8), the radioactivity was reduced by a factor of 15.

The workpiece was then charged to the furnace assembly which consisted of the silicon carbide crucible and tungsten carbide insulation held in place by a Fiberfrax lid on the crucible. The crucible was supported by a Lava stand adjustable vertically. The assembly was heated

by a 5-turn water-cooled copper induction coil made of flattened 1/2-in.-diameter copper tubing. Power was supplied by either a 30-kW or a 15-kW high-frequency (10-kc) motor generator.

Prior to being heated, the vacuum tank was evacuated to a pressure of less than 1μ by use of the Stokes Microvac roughing pump and diffusion pump.

When a suitable vacuum (about 1μ) had been obtained, the motor generator was started and the high-frequency power was turned on at such a value of power input that the rate of degassing of the insulation would not cause excessive pressure rise. The furnace assembly was heated to a desired temperature; when a constant temperature was attained, readings were taken every 5 min of (1) activity emanating from the vapor phase, (2) activity emanating from the liquid phase, and (3) temperature measured by the tungsten-5% rhenium/tungsten-26% rhenium thermocouples. At least four separate 5-min counts were taken of the activity from each phase.

When sufficient data had been taken at any one temperature, the power input was increased and the data-taking procedure was repeated at the new higher temperature.

As soon as a run was completed, the power was turned off and the unit cooled to room temperature. The furnace assembly was then removed from the vacuum tank and disassembled, and a new charge was made.

Safety Measures

To conclude the description of the various operations, the safety aspects of the experimental work will be discussed.

The alkali metals react rapidly with moisture and/or air. Consequently, whenever these metals are exposed, the atmosphere must be of high purity, i.e., low in water and oxygen content. For this reason all charging operations were done in a high-purity helium atmosphere glove-box. Excess alkali metal was neutralized with butanol to convert to a non-reactive form.

Alkali metals have very high vapor pressures when heated to the critical-temperature region (of the order of 200 to 700 atm) so that the equipment had to be designed to contain these pressure forces. The original design of the capsule-holding piece had safety factors of 2 to 4; the revised design had safety factors of 5 to 10.

The principal hazard in the experimental work was the appreciable levels of radioactivity being handled. When the irradiated capsule came back from the reactor in a lead-shielded pot, not only was the alkali metal radioactive but also the container material (Mo-30 w/o W). The capsule

was cooled up to 30 days, depending on the half-life of the alkali metal. After cooling for 30 days, the activity at the surface of the capsule was of the order of 10 R/hr for an irradiated cesium sample, for example.

The capsule was then charged to the Mo-30 w/o W sample holder by means of long tongs, working rapidly so as to keep the time factor to a minimum. Surgeon's gloves, film badges, and dosimeters were worn for this operation. Radiation Safety representatives monitored all transfer operations.

After the capsule was charged to the cylindrical block sample holder, the sample holder was charged to the furnace assembly. The dense sample holder, the tungsten carbide powdered insulation, and the silicon carbide crucible reduced the activity level by a factor of 10 to 20 from the measured capsule surface activity to that at the crucible surface, depending on the energy level of the alkali metal gamma rays. The furnace assembly was then charged to the vacuum tank. The vacuum tank lid was then closed and the vessel pumped down to a pressure of about 1μ prior to heating with the induction coil.

As the capsule was heated from room temperature to the critical point, the vapor- and liquid-phase activities were measured by means of the single-channel analyzer. If a capsule broke, the counters would immediately show a 100-fold increase in activity, and the vacuum system and induction heating would be immediately shut off. The most hazardous operation in cleaning up after a capsule failure was in moving the furnace assembly (the silicon carbide crucible which contains the insulation, tantalum can, and the Mo-30 w/o W block containing the ruptured capsule) from the vacuum tank to a hood where the furnace assembly was placed in a cave made of shielding blocks. The radiation level at the surface of the crucible was a maximum of 500 to 750 mR/hr. Subsequent operations were then performed from behind shielding in the ventilated hood. This operation was performed several times without incident. The transfer was made by three people working in series, one to remove the crucible assembly from the vacuum furnace, one to bag it in a plastic bag, and one to transfer the bagged crucible to the cave in the hood. Appropriate safety equipment was worn (paper coveralls, assault masks, rubber gloves, monitoring meters, and badges), the transfer path was covered with plastic, and all operations were monitored. The entire transfer could be made in 2 or 3 min so that the activity pick-up by personal was minimal (maximum pick-up 2 to 5 mR).

After the furnace assembly was removed, the activity level outside the vacuum tank dropped sharply, so that normal work operations could be resumed in the area. Subsequent cleanup of the inside walls of the stainless steel vacuum tank indicated no problem of airborne activity and usually required less than a day to reduce contamination to a fixed level so that there was no measureable radiation coming through the walls of the tank. All

operations were monitored, however, for maximum safety. Radioactive capsules, crucibles, and powder insulation were discarded in suitable containers according to their activity level.

Analyses of High-purity Alkali Metals

The manufacturers' analyses of high-purity cesium, rubidium, sodium, and potassium are shown in Table 8. The material of highest purity was potassium, although alkali metal impurities were not reported for this

TABLE 8. Manufacturers' Analyses of High-purity Alkali Metals

Impurity Element	Impurity Concentration, ppm			
	Cesium	Rubidium	Sodium	Potassium
K	7	300	100	-
Na	<16	40	-	-
Li	18	90	-	-
Rb	35	-	25	-
Cs	-	500	15	-
Al	<2	<1	2	2
Ca	18	<1	-	1
Cr	<2	30	<1	3
Cu	<2	10	<1	3
Fe	<14	<100	2	1
Pb	<2	1	<5	4
Mg	5	<1	<1	5
Mn	5	<1	<1	1
Ni	<2	10	<1	2
Tl	-	-	-	-
Ti	<2	-	<5	10
Bu	8	-	<3	-
B	<18	-	<5	10
Si	<4	<1	10	10
Sn	8	-	<5	1
Sr	<2	-	<1	-
O	11	100	-	-
Cl	-	-	20	-
P	-	-	10	-
S	-	-	20	-
Be	-	-	<1	1
Mo	-	-	<5	1
V	-	-	<1	2
Ag	-	-	<1	1
Co	-	-	<5	5
Zr	-	-	<10	-
Total	181	1306	261	63

metal. Rubidium and cesium were analyzed by Argonne National Laboratory's Chemistry Division (with an emission spectrograph). The cesium analysis agreed very closely with the manufacturer's analysis, but the cesium content of the rubidium, 1000 ppm, was double the manufacturer's analysis.

Cheng⁴⁸ has reported on the effects of impurities on the critical temperature. For binary systems, these effects may be expressed as follows:

$$(T_c)_{\text{measured}} = X_1(T_c)_1 + X_2(T_c)_2 + X_1X_2\theta_{12}, \quad (14)$$

where

T_{c1} = critical temperature of component 1;

T_{c2} = critical temperature of component 2;

X_1 = atomic fraction of component 1;

X_2 = atomic fraction of component 2;

θ_{12} = interaction temperature (experimentally determined).

For all the systems and concentrations studied by Cheng, θ_{12} was less than the critical temperature of either component. So a conservative approximation of θ_{12} is the average of the critical temperatures of the two components. If $(T_c)_1$ is the desired critical temperature and $(T_c)_2$ is known, Equation (14) can be solved for $(T_c)_1$, giving

$$(T_c)_1 = \frac{(T_c)_{\text{measured}} - X_2(T_c)_2 - X_1X_2\theta_{12}}{X_1} \quad (15)$$

Now if

$$\theta_{12} = \frac{1}{2}[(T_c)_1 + (T_c)_2],$$

Equation (15) becomes

$$(T_c)_1 = \frac{(T_c)_{\text{measured}} - X_2(T_c)_2 - \frac{1}{2}X_1X_2(T_{c1} + T_{c2})}{X_1} \quad (16)$$

Upon solving (16) for $(T_c)_1$, we obtain

$$(T_c)_1 = \frac{(T_c)_{\text{measured}} - X_2(T_c)_2 - \frac{1}{2}X_1X_2(T_c)_2}{X_1} \quad (17)$$

This enables us to correct the measured temperature for the effect of a major impurity. For the systems being measured and the expected concentrations of impurities, the correction would be less than the expected error in the measurement of the critical temperature.

CHAPTER IV

EXPERIMENTAL RESULTS

Experimental data are presented in this section. Vapor- and liquid-density data are presented, and various methods of correlating them in order to obtain accurate estimates of critical densities are described. These correlating methods include "Kordes group" plots, Rowlinson-type logarithmic temperature-density plots, rectilinear diameter density-temperature plots, and the generalized correlation of reduced density with reduced temperature. From these correlations, values of critical temperature and critical density are derived. From an estimate of the critical pressures, compressibility factors are calculated.

Vapor and Liquid Densities

Vapor and liquid densities were obtained from room temperature up to or near the critical temperature for sodium, cesium, and rubidium. For potassium, the low abundance of the precursor of the radioactive isotope, the low percent of desired gamma activity, and the short half-life made it difficult to obtain data above 1200°C. Vapor and liquid densities of the four alkali metals studied are given in Tables 9 to 12. Typical data for a sodium run are given in Appendix B, page 55. These data were correlated by plotting both vapor and liquid densities on a rectilinear diameter plot of density versus temperature (see Figs. 11 to 14).

TABLE 9. Saturated Vapor and Liquid Densities of Sodium

Run No.	Capsule No.	Weight of Sodium, g	Temperature, °C	Liquid Density, g/cc	Vapor Density, g/cc
Na-2	11 ^a	0.0789	895	0.757	0.0026
Na-2	11	0.0789	1190	0.667	0.0266
Na-3	11	0.0789	1455	0.602	0.0077
Na-3	11	0.0789	1543	0.562	0.0138
Na-4	11	0.0789	1584	0.557	0.0261
Na-4	11	0.0789	1640	0.537	0.0128
Na-4	11	0.0789	1693	0.546	0.0288
Na-4	11	0.0789	1718	0.532	0.0397
Na-4	11	0.0789	1754	0.512	0.0437
Na-7	10 ^b	0.0933	1850	0.506	0.0370
Na-7	10	0.0933	1928	0.502	0.0520

^aMolybdenum-30 w/o tungsten capsule irradiated 10 hr at a thermal-neutron flux of 5×10^{-12} n/(cm²)(sec).

^bMolybdenum-30 w/o tungsten capsule irradiated 12 hr at a thermal-neutron flux of 5×10^{12} n/(cm²)(sec).

TABLE 10. Saturated Vapor and Liquid Densities of Cesium

Run No.	Capsule No.	Weight of Cesium, g	Temperature, °C	Liquid Density, g/cc	Vapor Density, g/cc
Cs-13	3 ^a	0.2608	600	1.501	0.0005
Cs-13	3	0.2608	704	1.455	0.0036
Cs-13	3	0.2608	863	1.380	0.0075
Cs-14	3	0.2608	866	1.370	0.0094
Cs-24	2 ^b	0.1977	885	1.360	0.0078
Cs-13	3	0.2608	955	1.293	0.0144
Cs-14	3	0.2608	997	1.279	0.0174
Cs-14	3	0.2608	1133	1.168	0.0301
Cs-23	2 ^b	0.1977	1142	1.200	0.0340
Cs-23	2 ^b	0.01977	1251	1.130	0.0500
Cs-21	2 ^c	0.1655	1340	1.060	0.0720
Cs-23	2 ^b	0.1977	1341	1.058	0.0690
Cs-24	2 ^b	0.1977	1354	1.050	0.0710
Cs-23	2 ^b	0.1977	1406	1.015	0.0840
Cs-23	2 ^b	0.1977	1445	0.980	0.0950
Cs-24	2 ^b	0.1977	1497	0.939	0.1050
Cs-21	2 ^c	0.1655	1505	0.961	0.1170
Cs-22	2 ^c	0.1655	1510	0.931	0.1190
Cs-29	2 ^b	0.1977	1515	0.843	0.147
Cs-22	2 ^c	0.1655	1565	0.972	0.1160
Cs-31	2 ^b	0.1977	1583	0.837	0.126
Cs-24	2 ^b	0.1977	1590	0.866	0.1730
Cs-31	2 ^b	0.1977	1593	0.638	0.1810
Cs-22	2 ^c	0.1655	1622	0.772	0.1640
Cs-31	2 ^b	0.1977	1635	0.600	0.212
Cs-24	2 ^b	0.1977	1649	0.751	0.2620
Cs-31	2 ^b	0.1977	1702	0.357	0.438
Cs-29	2 ^b	0.1977	1718	0.509	0.478
Cs-29	2 ^b	0.1977	1770	0.509	0.478
Cs-32	15 ^d	0.1638	1163	1.202	0.029
Cs-32	15 ^d	0.1638	1252	1.123	0.038
Cs-32	15 ^d	0.1638	1344	0.993	0.050
Cs-32	15 ^d	0.1638	1465	0.898	0.069
Cs-32	15 ^d	0.1638	1505	0.842	0.079

^a Molybdenum-30 w/o tungsten capsule irradiated 30 days at a flux of 5×10^{12} n/(cm²)(sec).

^b The 98 w/o tungsten-2 w/o molybdenum capsule was irradiated 32 hr at a flux of 5×10^{13} n/(cm²)(sec).

^c Molybdenum-30 w/o tungsten capsule irradiated 2 days at a flux of 5×10^{13} n/(cm²)(sec).

^d Molybdenum-30 w/o tungsten capsule irradiated 3 days at a flux of 5×10^{13} n/(cm²)(sec).

TABLE 11. Saturated Vapor and Liquid Densities of Rubidium

Run No.	Capsule No.	Weight of Rubidium, g	Temperature, °C	Liquid Density, g/cc	Vapor Density, g/cc
Rb-4	1 ^a	0.2200	870	1.095	0.0040
Rb-4	1	0.2200	1040	1.090	0.0080
Rb-4	1	0.2200	1250	0.900	0.0230
Rb-5	1	0.2200	1310	0.935	0.0360
Rb-4	1	0.2200	1360	0.881	0.0330
Rb-6	1	0.2200	1402	0.874	0.0630
Rb-5	1	0.2200	1420	0.845	0.0530
Rb-6	1	0.2200	1502	0.766	0.0830
Rb-6	1	0.2200	1564	0.724	0.0950
Rb-6	1	0.2200	1603	0.707	0.1050
Rb-6	1	0.2200	1656	0.640	0.1350
Rb-6	1	0.2200	1720	0.568	0.1680
Rb-8	14 ^b	0.1723	970	1.032	0.0025
Rb-8	14	0.1723	1178	0.911	0.0144
Rb-8	14	0.1723	1336	0.877	0.0321
Rb-8	14	0.1723	1438	0.804	0.0530
Rb-8	14	0.1723	39	1.580	-

^aMolybdenum-30 w/o tungsten capsule irradiated 10 days at a flux of $5 \times 10^{13} \text{ n}/(\text{cm}^2)(\text{sec})$.

^bMolybdenum-30 w/o capsule tungsten irradiated 20 days at a flux of $5 \times 10^{13} \text{ n}/(\text{cm}^2)(\text{sec})$.

TABLE 12. Saturated Vapor and Liquid Densities of Potassium

Run No.	Capsule No.	Weight of Potassium, g	Temperature, °C	Liquid Density, g/cc	Vapor Density, g/cc
K-3	17 ^a	0.0635	898	0.627	0.0035
K-3	17	0.0635	1004	0.606	0.0067
K-3	17	0.0635	1097	0.584	0.0111
K-3	17	0.0635	1202	0.560	0.0383

^aMolybdenum capsules irradiated 4 days at a thermal-neutron flux of $5 \times 10^{13} \text{ n}/(\text{cm}^2)(\text{sec})$.

Fig. 11
Density and Rectilinear
Diameter Plot for Cesium

Fig. 12. Density and Rectilinear Diameter Plot for Rubidium

Fig. 13. Density and Rectilinear Diameter Plot for Sodium

Fig. 14

Density and Rectilinear
Diameter Plot for Postassium

From such plots, estimates of the critical density and critical temperature can be made. It is then possible to make the correlation suggested by Rowlinson.⁵⁸ For the vapor-density data, this consists of a graph of $\ln(\rho_c - \rho_v)$ versus $\ln(T_c - T)$. For the range $(T_c - T) = 250^\circ\text{C}$ to the critical point $[(T_c - T) = 0]$, this should be a straight line of slope about 0.4. These correlations are shown in Fig. 15.

Fig. 15. Vapor-density Difference-Temperature
Difference Correlations

A similar correlation of $\ln(\rho_L - \rho_c)$ versus $\ln(T_c - T)$ may be made for the liquid data. This correlation is good for a range up to 450°C below the critical temperature. These are presented graphically in Fig. 16.

An additional correlation may be made to show the interaction of vapor and liquid densities. This is a correlation of $\ln(\rho_L - \rho_v)$ versus $\ln(T_c - T)$. These three correlations are based on the corresponding-state equations of Guggenheim given in Chapter I. The equations needed for the correlations are derived in Appendix C. The liquid density-vapor density correlation is presented in Fig. 17.

Fig. 16

Liquid-density Difference-Temperature Difference Correlation

Fig. 17. Liquid-density-Vapor-density Difference-Temperature Difference Correlation

A "Kordes group" plot⁶⁶⁻⁶⁸ is also an excellent way of predicting critical temperature. This plot of $\log_{10} \frac{4\rho_v\rho_L}{(\rho_L + \rho_v)^2}$ versus $\log_{10} t$ is based on

empirical correlations. The term

$$4\rho_v\rho_L/(\rho_L+\rho_v)^2$$

becomes 1.0 at $t = t_c$ as shown in Fig. 18.

Fig. 18. Kordes Plot for Estimating Critical Temperature

A generalized correlation for plotting the density data was developed and is shown in Fig. 19. This is a plot of reduced density versus reduced temperature. Data obtained for the alkali metals examined in this study all fall on one line, as may be seen from examination of Fig. 19. In addition, liquid-density data for lithium⁸⁵ have been used to estimate critical constants for lithium by means of a combination of the generalized correlation, the Kordes plot, and the rectilinear diameter plot. These data are plotted on Figs. 18 and 19.

Fig. 19. Generalized Correlation of Reduced Density with Reduced Temperature for Alkali Metals

Predictions of critical temperatures and critical densities were made from the correlations mentioned above. Error limits on the critical temperatures were established as follows: A least-squares fit to the straight-line equation of the Kordes plot was made, and error limits at $NK_0 = 1$ were calculated from regression analysis. The error given is the 95% confidence level (2.05 times the standard deviation). Assuming the rectilinear-diameter line is straight, the corresponding error in critical density can be obtained from Figs. 11 through 14. Critical constants and data on error limits for critical temperature, critical density, critical volume, and critical compressibility factor are given in Table 13.

TABLE 13. Critical Temperatures and Critical Densities for Alkali Metals Obtained in This Work and Estimated Critical Compressibility Factors

Alkali Metal	Atomic Weight	Critical Temperature T _c , °K	Critical Density ρ _c , g/cc	P _c , atm ^e	V _c , liter/g-mole	Critical Compressibility Factor, Z _c ^f	Ratio of Critical Temperature to Boiling Point, T _c /T _B
Lithium	6.94	3223 ± 600 ^g	0.120 ± 0.033	680	0.066 ± 0.019	0.17 ± 0.12	2.02
Sodium	22.99	2573 ± 350 ^c	0.206 ± 0.041	350	0.116 ± 0.023	0.20 ± 0.12	2.23
Potassium	39.10	2223 ± 330 ^d	0.194 ± 0.037	160	0.209 ± 0.040	0.21 ± 0.13	2.16
Rubidium	85.47	2093 ± 35 ^b	0.346 ± 0.009	157	0.247 ± 0.007	0.22 ± 0.02	2.20
Cesium	132.9	2057 ± 40 ^a	0.428 ± 0.012	145	0.311 ± 0.008	0.25 ± 0.02	2.15

^aBased on data to 1650°C.

^bBased on data to 1720°C.

^cBased on data to 1930°C.

^dBased on data to 1202°C.

^eEstimated error ±20%.

^fZ_c = P_cV_c/RT_c.

^gBased on liquid density data to 1200°C.⁸⁵

Predictions of critical temperatures and critical densities have been made by Grosse⁹ and by Hochman and Bonilla.^{56,57} The data obtained in this work gave values of critical temperatures which were higher than the values predicted by Hochman and Bonilla and lower than the values predicted by Grosse, but all were well within the error range given for their estimates.

No vapor pressures of the alkali metals were obtained. However, estimates of the critical pressure were made by extrapolation of present vapor pressure data. This then enables calculation of critical compressibility factors within the error of the pressure estimates ($\pm 20\%$); the critical compressibility factors of the alkali metals all fell in the same range (0.22 ± 0.05).

Critical temperatures are sometimes estimated from the normal boiling point by multiplying by an appropriate constant (2.75 for mercury). The ratio of critical temperature to normal boiling point for the alkali metals is given in Table 13 and appears to be about 2.2.

CHAPTER V

DISCUSSION OF RESULTS

The results obtained in this investigation were compared with low-temperature ($<1200^{\circ}\text{C}$) density data from the literature for all systems and with high-temperature density data (up to 1650°C) obtained for cesium only. Critical temperatures obtained in this investigation were compared with estimates of other investigators. A statistical analysis of the density data for cesium has been made. Density data for mercury are presented and heats and entropies of vaporization of mercury are compared with similar properties calculated for alkali metals. Based on the data of this study, second and third virial coefficients have been calculated for cesium and compared with those estimated by other investigators.

Comparison of Experimental Data on Cesium and Rubidium with the Results of Hochman and Bonilla^{56,57,69} and Other Investigators^{9,60-62,65,70,71}

Hochman and Bonilla^{56,57,69,83} estimated the critical temperatures, critical pressures, and critical densities of rubidium and cesium based on electrical conductivity measurements to 3000°F for cesium and 2900°F for rubidium. Hochman and Bonilla found the volumes of the liquid and vapor phases of cesium by passing direct current lengthwise along a tube and locating the liquid level by the IR drop. The test was carried out with three known weights of cesium and to temperatures of 3000°F . In a recent paper⁸³ they estimate the critical temperature of cesium to be 1723°C . Previously they estimated the critical temperature of cesium to be 3190°F (1754°C). In an earlier paper⁵⁶ they estimated the critical point to be 1783°F . They predict⁸³ the critical pressure to be 123 atm and the critical density to be 0.45 g/cc. The vapor and liquid densities obtained for cesium in this investigation are compared with the values of Hochman and Bonilla⁶⁹ in Table 14. In this work the critical temperature is taken to be 1784°C and the critical density as 0.428 g/cc. As may be seen in Table 14, Hochman and Bonilla's smoothed liquid densities for cesium agree very well with the data of this

TABLE 14. Comparison of Observed Vapor and Liquid Densities for Cesium with the Results of Hochman and Bonilla⁶⁹

Temperature $^{\circ}\text{C}$	Vapor Density, g/cc			Liquid Density, g/cc		
	This Study	Hochman and Bonilla		This Study	Hochman and Bonilla	
		Experimental Data	Smoothed Data		Experimental Data	Smoothed Data
1055	0.025	-0.005	0.001	1.250	1.276	1.250
1220	0.043	0.006	0.010	1.142	1.208	1.136
1325	0.065	0.047	0.024	1.080	1.084	1.063
1437	0.090	0.060	0.050	0.990	1.022	0.980
1551	0.120	0.068	0.092	0.895	0.962	0.899
1640	0.170	0.140	0.150	0.785	0.830	0.829

study. The point differing to the greatest extent is at 1640°C, and this is within the $\pm 5\%$ error of the method of Hochman and Bonilla. The vapor densities of Hochman and Bonilla are consistently lower than those from this study.

The liquid densities obtained in this study agree with density data reported by other investigators,^{60-62,65,70,71,83} although liquid densities were reported up to a reduced temperature of only 0.6.

The estimate of Hochman and Bonilla^{57,83} for the critical temperature of rubidium was 1828°C. In this study, we found 1820°C to be the critical temperature.

Grosse's estimates⁹ of critical densities and critical temperatures are given in Table 5. In general his estimates are somewhat higher than our values, but well within the error range given for his estimates.

Morris⁷² has applied the theory of corresponding states to predict the critical constants of metals (see Table 15). The estimates of Bonilla and Grosse are also given in this table.

TABLE 15. Comparison of Predictions of Critical Constants of the Alkali Metals and Mercury with the Experimental Results of This Study and the Data of Hochman and Bonilla

Metal	Critical Temperature T_c , °K				Critical Pressure P_c , atm			Critical Volume V_c , liter/g-mole		
					Equation of Sawhney and Bonilla ¹⁴ Based on T_c of This Study					
	This Study	Morris ⁷²	Grosse ⁹	Hochman and Bonilla ^{56,57,83}		Morris ⁷²	Grosse ⁹	This Study	Morris ⁷²	Grosse ⁹
Li	3223	4400	4110	-	680 ^a	1330	-	0.066	0.088	-
Na	2573	2800	2780	-	350	510	490	0.116	0.150	0.128
K	2223	2300	2440	-	160	250	240	0.209	0.240	0.217
Rb	2093	2100	2190	2111	157	175	180	0.247	0.320	0.267
Cs	2057	2000	2150	1996	145	140	170	0.311	0.380	0.316

^aEquation of Maucherat.^{87,88}

Statistical Analysis of Data

Two types of statistical analysis were made. First, the data were analyzed for reproducibility. Replicate runs were made for cesium, as may be seen from Table 10, at 865, 1135, 1340, and 1510°C within $\pm 10^\circ\text{C}$. For the liquid densities the standard deviation is ± 0.015 in the range from 0.931 to 1.200 g/cc, which is an error of about $\pm 1.5\%$. For the vapor densities, the standard deviation is 0.0015 in the range from 0.0075 to 0.1190 g/cc, which is an error of about $\pm 20\%$ in the lower end of the range to $\pm 2\%$ in the higher end of the range. These errors are affected also by the background level for counting. A desirable level for counting is at least twice background level and preferably higher. This contributed to the high error level in measuring vapor densities at temperatures well below the critical temperature.

The second type of analysis was a chi-squared test on the counting data⁸⁶ to assure that it was sufficiently random. The correlation coefficient averaged about 0.6, which shows that the data were consistent but not biased.

Calculation of Heat of Vaporization from Vapor and Liquid Densities

Grosse⁹ used data for mercury to predict critical temperatures of many metals. Density data for mercury are given in Table 1 and are plotted on a rectilinear diameter plot in Fig. 20.

Fig. 20. Rectilinear Diameter Plot for Mercury

Vapor and liquid density data may be used to calculate heats of vaporization if data are available for the vapor pressures of the materials. Although no data were available for the vapor pressures of the alkali metals near the critical point, Bonilla *et al.*¹⁴ have obtained data to 25 atm and have presented vapor pressure equations for all four alkali metals investigated experimentally in this study. These equations, therefore, may be used for extrapolation to higher temperatures. The necessary expression may be derived from the Clapeyron equation as follows:

The Clapeyron equation is

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(V_g - V_l)}, \quad (18)$$

where

ΔH_v = heat of vaporization, liter-atm/g-mole;

T = temperature, °K;

V_g = molar volume of saturated vapor, liters/g-mole;

V_l = molar volume of saturated liquid, liters/g-mole;

P = vapor pressure of saturated phases in equilibrium, atm.

The form of the vapor pressure equations given by Sawhney and Bonilla is

$$\log_{10} P = A - (B/T), \quad (19)$$

where A and B are constants. Multiplying by 2.303 to convert to natural logarithms,

$$2.303 \log_{10} P = \ln P = 2.303A - (2.303B/T). \quad (20)$$

Differentiating Equation (20) with respect to temperature, we obtain

$$\frac{1}{P} \frac{dP}{dT} = \frac{2.303B}{T^2} \quad (21)$$

which yields

$$\frac{dP}{dT} = \frac{2.303BP}{T^2}. \quad (22)$$

Substituting (22) in the Clapeyron equation and solving for ΔH_V , we obtain

$$\Delta H_V = \frac{2.303BP}{T} K[(V_g - V_l)], \quad (23)$$

where K is a conversion factor equal to 24.218 cal/liter-atm.

Equation (23) was used to calculate heat of vaporization data for the alkali metals. Heats of vaporization were plotted as $\log \Delta H_V/RT_C$ vs. $\log (1 - T_r)$ in Fig. 21, as suggested by Martin and Edwards.⁷³ This plot

does not agree with the prediction of Martin and Edwards that these curves should be parallel depending only on M, the slope of the vapor pressure curve at the critical point.

Fig. 21. Heats of Vaporization for the Alkali Metals and Mercury

Grosse made a plot of entropy of vaporization ($\Delta H_V/T$) vs. reduced temperature, using known heats of vaporization for mercury. He then used this curve and the heats of vaporization of other materials at their boiling point to predict critical temperatures. Such curves for mercury, water, and alkali metals are shown in Fig. 22.

Fig. 22. Variation of Entropy of Vaporization with Reduced Temperature for Alkali Metals, Mercury, and Water

Figure 22 may be used to estimate the critical temperature of lithium as follows. If at one atmosphere pressure lithium boils at the same reduced temperature as sodium, the estimated critical temperature of lithium would be 3540°K. This compares with a value of 3223°K obtained from the generalized correlation of Fig. 19.

Equations of State

The pressure-volume-temperature relationships of ideal gaseous systems may be represented by the ideal-gas law:

$$PV = nRT. \quad (24)$$

For actual systems, a more complicated equation of state is usually needed, e.g., one using virial coefficients, such as Equation (7). For most engineering work the second virial coefficient is sufficient (up to $P_r = 0.5$). For conditions near the critical region,

at least the third virial coefficient is necessary to make accurate predictions of thermodynamic properties.⁷⁴ With the inclusion of the third virial coefficient, Equation (7) becomes

$$\frac{P\tilde{V}}{RT} = 1 + \frac{B}{\tilde{V}} + \frac{C}{\tilde{V}^2}. \quad (25)$$

Inasmuch as

$$\tilde{V} = M/\rho, \quad (26)$$

we have

$$\frac{PM}{RT\rho} = 1 + \frac{B\rho}{M} + \frac{C\rho^2}{M^2}. \quad (27)$$

Upon multiplying Equation (27) by ρM^2 , we obtain

$$PM^3/RT = \rho M^2 + B\rho^2 M + C\rho^3, \quad (28)$$

where B and C are functions of T . For a given set of conditions of pressure and temperature, Equation (28) is a cubic equation in ρ . We know M and we have ρ from the data of this study.

As an example, we use smoothed data for cesium to calculate virial coefficients from Equation (7). The forms assumed for the values of the virial coefficient were as follows:

$$\log_{10} (-B) = B_0 + \frac{B_1}{T} + \log_{10} T; \quad (29)$$

$$\log_{10} C = C_0 + \frac{C_1}{T} + \frac{C_2}{T^2}. \quad (30)$$

These coefficients were evaluated for cesium from the data at 900, 1000, 1400, and 1600°K. The resulting equations for the virial coefficients were

$$\log_{10} (-B) = -1.904 + \frac{2580}{T} + \log T; \quad (31)$$

$$\log_{10} C = 3.422 - \frac{2530}{T} + \frac{7.83 \times 10^6}{T^2}. \quad (32)$$

Coefficients calculated from these equations are compared with those calculated by Ewing⁷⁹ and Miller⁸⁰ in Table 16. The third virial coefficients do not agree too well with the calculations of Ewing. This may be partially due to the fact that the vapor pressures used are an extrapolation and may be subject to error.

TABLE 16. Comparison of Values of Virial Coefficients for Cesium Found in This Study with Those of Ewing⁷⁹ and Miller⁸⁰

Temperature, °K	Second Virial Coefficient "B"			Third Virial Coefficient "C"		
	This Study	Ewing	Miller	This Study	Ewing	Miller
1000	-4750	-4245	-4140	5.29×10^8	1.37×10^7	-
1500	-980	-1317	-965	1.65×10^5	3.52×10^6	-
2000	-485	-800	-463	1.32×10^4	2.50×10^6	-

CHAPTER VI

CONCLUSIONS

General Conclusions

1. The critical temperatures of the alkali metals were obtained by measurements of vapor and liquid densities up to nearly the critical point and then extrapolating the data by use of Kordes' plot.⁶⁶ This is a

plot of $\log \frac{\rho_v \rho_L}{\left(\frac{\rho_v + \rho_L}{2}\right)^2}$ vs. $\log t$, which gives a straight line with intercept t_c at

$$\frac{\rho_v \rho_L}{\left(\frac{\rho_v + \rho_L}{2}\right)^2} = 1.0.$$

These estimates were then smoothed by use of the generalized correlation of Fig. 19. Estimates of critical temperatures obtained by this method compared favorably with those obtained by the technique of Rowlinson (see Figs. 15-17), which is based on an extension of corresponding-state theory.

The alkali metals do not obey corresponding-state theory precisely in that the exponent n of the $(1 - T_r)$ term in

$$\rho/\rho_c = 1 + A(1 - T_r) \pm B(1 - T_r)^n \quad (33)$$

does not agree with theory; instead of having the value $1/3$ predicted by Guggenheim²³ from corresponding-state theory, or the value $5/16$ predicted by Fischer⁸² for lattice gas theory, the value of n is about 0.4 for the vapor, and 0.5 to 0.7 for the liquid. Also, B is not equal to $A + 1$ in fitting Equations (1) and (2) to the density data obtained.

2. The method used in this study for obtaining vapor and liquid densities to very high temperatures is general in nature and applicable to the determination of vapor and liquid density for almost any substance that does not decompose or react chemically at the measuring temperature. If the substance were not activated by neutron irradiation, a radioactive trace of the substance being tested might be added, or an attenuation method might be used; this would involve a radioactive source and directing a collimated beam of radiation through the material. The equipment used in this investigation is relatively simple although not inexpensive.

Suggestions for Future Work

Additional work in this field could include obtaining more data near and above the critical point. This would include finding perhaps a better capsule design as well as better materials of construction. An important contribution could be made by determining vapor pressures of the alkali metals all the way to the critical point. Also, data on the densities of lithium could be obtained even if it were not possible to obtain data all the way to the critical point. High-temperature densities of other materials could be obtained including metals, fused salts, and mixtures such as the mercury-potassium system, which is of interest for magnetohydrodynamic (MHD) systems and also for mobile compact reactors. This mixture should have a pseudo-critical point below that of potassium. All these suggested areas of additional work would contribute toward theoretical understanding and also toward many applications of current interest.

APPENDIX A

Effect of Self-shielding on the Counting Rate

If self-shielding were appreciable, this would materially affect readings of activity at the counter, a single-channel analyzer. Therefore, expressions have been developed to take this into account.

First, let us develop an expression for no self-shielding. For this case, the activity at the source is proportional to density, i.e.,

$$A_s = b\rho, \quad (34)$$

where

A_s = activity at source;

b = proportionality constant;

ρ = density, g/cc.

This activity is reduced by attenuation, geometry, distance, etc., so that activity at the counter is given by the following expression:

$$A_c = (b\rho/K)(e^{-\mu_{MoW}\rho_{MoW}X_{MoW}})(e^{-\mu_{SST}\rho_{SST}X_{SST}}), \quad (35)$$

where

A_c = activity at counter;

K = reduction of activity due to various factors other than attenuation;

μ_{MoW} = gamma-ray absorption coefficient of MoW alloy, cm^2/g ;

X_{MoW} = thickness of MoW wall, cm;

μ_{SST} = gamma-ray absorption coefficient of stainless steel alloy, cm^2/g ;

X_{SST} = thickness of stainless steel, cm.

Since the stainless steel is essentially at room temperature, and the density of MoW varies only slightly with temperature, the exponential terms may be assumed constant, and we obtain

$$A_c = R\rho, \quad (36)$$

where

$$R = (b/K) \exp[-(\mu_{MoW}\rho_{MoW}X_{MoW} + \mu_{SST}\rho_{SST}X_{SST})],$$

or

$$\rho = A_c/R = cA_c. \quad (37)$$

For self-shielding,

$$A_c = R\rho f, \quad (38)$$

where f is a self-shielding factor equal to the fraction of activity escaping. It has been shown* that

$$f = 1 + a\xi + b\xi^2, \quad (39)$$

where for cylinders

$$\xi = \sigma r = \mu r \rho \quad (40)$$

and

μ = gamma-ray absorption coefficient, cm^2/g ;

r = radius of cylinder, cm ;

ρ = density of material, g/cm^3 .

Substituting (57) in (56), we obtain

$$f = 1 + a\mu r \rho + b\mu^2 r^2 \rho^2 \quad (41)$$

or, for constant μ and r ,

$$f = 1 + a'\rho + b'\rho^2. \quad (42)$$

Substituting (42) in (38), we obtain

$$A_c/R = b'\rho^3 + a'\rho^2 + \rho, \quad (43)$$

where

$$a' = a\mu r; \quad b' = b\mu^2 r^2.$$

Equation (43) may readily be solved for ρ by use of numerical techniques and a computer.

Consider the case of mercury, which will enable us to see the range of values for the coefficients. For mercury over the range of ρ from 4.7 to $13.6 \text{ g}/\text{cm}^3$, Equation (42) becomes

*See KAPL-732, p. 71.

$$f = 1 - 0.092\rho + 0.0032\rho^2. \quad (44)$$

At the critical density of mercury ($\rho = 4.7$ g/cc)

$$f = 1 - 0.092(4.7) + 0.0032(4.7)^2 = 0.639.$$

In other words, 36% of the activity is not counted. At room temperatures ($\rho = 13.6$ g/cc)

$$f = 1 - 0.092(13.6) + 0.0032(13.6)^2 = 0.34,$$

that is, 66% of activity is not counted.

For the alkali metals, the density is less by at least a factor of ten, and the gamma energy is higher. Both of these factors combine to decrease self-shielding.

APPENDIX B

Typical Data for a Sodium Run (Na-7)1. Sodium Standard

A sodium standard consisting of C.P. NaNO_3 crystals was irradiated in a thermal-neutron flux and its spectrum scanned to determine the location of the 1.38-MeV and higher-energy peaks. The sodium sample was then counted at a window level such that only the sodium activity would be counted. Activity levels were converted to density by a comparative method to avoid the problems attendant on an absolute method.

2. Activity of Vapor Phase

Temp, °C	Run Time, min	Gross Activity, ^a cpm	Decay Correction Factor ^b	Corrected Activity, ^c cpm	Background Correction, ^d cpm	Net Activity, cpm
1660	2,860	1,680	8.20	12,673	11,750	923
1850	2,915	1,700	8.50	13,330	11,750	1,580
1928	2,940	1,737	8.70	13,985	11,750	2,235

^aBased on the average of 4 five-minute counts.

^bDecay Correction Factor = $e^{\lambda t}$, where λ , the decay constant for sodium is $7.35 \times 10^{-4} \text{ min}^{-1}$, and t is the run time in minutes.

^cCorrected Activity = Gross Activity times Decay Correction Factor.

^dThis is a high background correction and leads to scatter in the data, since accuracy is probably only about $\pm 12\%$ for vapor and $\pm 2\%$ for liquid.

3. Activity of Liquid Phase

Temp, °C	Run Time, min	Gross Activity, cpm	Decay Correction Factor	Corrected Activity, cpm	Background Correction, cpm	Net Activity, cpm
1,190	0	40,050	1.00	40,050	11,750	28,300
1,660	2,860	4,200	8.20	33,573	11,750	21,823
1,850	2,915	4,054	8.50	33,243	11,750	21,493
1,928	2,940	3,932	8.70	33,063	11,750	21,313

4. Conversion of Activities to Densities

A survey of the literature showed the sodium liquid densities of Stone *et al.*⁶⁵ to be the most consistent. Stone *et al.* give the liquid sodium density at 1190°C as 0.667 g/cc. We thus obtain a conversion factor of

$$\frac{0.667 \text{ g/cc}}{28,300 \text{ cpm}} = 2.36 \times 10^{-5} \frac{\text{g/cc}}{\text{cpm}}$$

The following table is then obtained.

Temp, °C	Vapor Density ρ_v , g/cc	Liquid Density ρ_L , g/cc	$(\rho_v + \rho_L)/2$, g/cc
1190	0.027	0.667	0.347
1660	0.022	0.516	0.269
1850	0.037	0.506	0.271
1928	0.052	0.502	0.279

APPENDIX C

Derivation of Equations Used in Correlating Density Data

From Chapter I we have the corresponding-state equations suggested by Guggenheim:

$$\frac{\rho_L}{\rho_c} = 1 + \frac{3}{4}(1 - T_r) + \frac{7}{4}(1 - T_r)^{1/3} \quad (45)$$

$$\frac{\rho_v}{\rho_c} = 1 + \frac{3}{4}(1 - T_r) - \frac{7}{4}(1 - T_r)^{1/3}. \quad (46)$$

If we multiply both equations by ρ_c and rearrange, we obtain

$$\rho_L - \rho_c = \frac{3}{4}\rho_c(1 - T_r) + \frac{7}{4}\rho_c(1 - T_r)^{1/3}; \quad (47)$$

$$\rho_v - \rho_c = \frac{3}{4}\rho_c(1 - T_r) - \frac{7}{4}\rho_c(1 - T_r)^{1/3}. \quad (48)$$

Now it may be observed that in the region near the critical point the quantity $(1 - T_r)$ is much less than one. It then follows that

$$(1 - T_r) \ll (1 - T_r)^{1/3}. \quad (49)$$

Thus the term $\frac{3}{4}\rho_c(1 - T_r)$ may be eliminated from Equations (47) and (48), and we obtain

$$\rho_L - \rho_c = \frac{7}{4}\rho_c(1 - T_r)^{1/3}; \quad (50)$$

$$\rho_c - \rho_v = \frac{7}{4}\rho_c(1 - T_r)^{1/3}. \quad (51)$$

In actual practice the constant in Equations (50) and (51) is not $\frac{7}{4}$ and the exponent is not $\frac{1}{3}$. Accordingly, we rewrite Equations (50) and (51) with arbitrary constants:

$$\rho_L - \rho_c = A(1 - T_r)^B; \quad (52)$$

$$\rho_c - \rho_v = C(1 - T_r)^D; \quad (53)$$

If we take the logarithm of Equation (52), we obtain

$$\log (\rho_L - \rho_c) = \log A + B \log (1 - T_r). \quad (54)$$

Now

$$1 - T_r = 1 - \frac{T}{T_c} = \frac{T_c - T}{T_c} \quad (55)$$

and

$$\log \left(\frac{T_c - T}{T_c} \right) = \log (T_c - T) - \log T_c. \quad (56)$$

Putting (55) and (56) in (54), we obtain

$$\log (\rho_L - \rho_c) = \log A/T_c^B + B \log (T_c - T). \quad (57)$$

Similarly, Equation (53) becomes

$$\log (\rho_c - \rho_v) = \log C/T_c^D + D \log (T_c - T). \quad (58)$$

If we add Equations (50) and (51), we obtain

$$\rho_L - \rho_v = \frac{14}{4} \rho_c (1 - T_r)^{1/3} \quad (59)$$

or, rewriting in general form,

$$\rho_L - \rho_v = E(1 - T_r)^n. \quad (60)$$

Taking logarithms of both sides and applying Equations (55) and (56), we obtain

$$\log (\rho_L - \rho_v) = \log E/T_c^n + n \log (T_c - T). \quad (61)$$

Equations (54), (58), and (61) are the bases of the three correlations.

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