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**AN ASSESSMENT OF THE MELTING,
BOILING, AND CRITICAL POINT DATA
OF THE ALKALI METALS**

Prepared for publication by

R. W. OHSE¹, J.-F. BABELOT¹, J. MAGILL¹ and M. TETENBAUM²

¹Commission of the European Communities Joint Research Centre,
Karlsruhe Establishment, Karlsruhe, FRG

²Argonne National Laboratory, Chemical Technology Division,
Argonne, Illinois, USA

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An assessment of the melting, boiling, and critical point data of the alkali metals *

Abstract - The measured melting, boiling and critical point data of the alkali metals are reviewed. Emphasis has been given to the assessment of the critical point data. The main experimental techniques for measurements in the critical region are described. The selected data are given. Best estimates of the critical constants of lithium are given.

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INTRODUCTION

The growing technological importance of alkali metals, mainly due to their specific advantages for high temperature application (section 3 *), has resulted in an increased demand for a reliable and consistent set of thermodynamic data. The rapidly increasing fuel costs and need for improved thermal efficiency of power plants consequently led to an increase in the peak temperatures of the cycles (chapter 3.1). The resulting necessity for safety risk assessment led to considerable efforts to extend our knowledge up to and even beyond their critical point temperatures.

In this chapter the measured melting, boiling and critical point data of the alkali metals are reviewed. The melting point temperatures are well established. Deviations within a degree or less are mainly due to the impurity content of the sample. Because of the somewhat large scatter in boiling temperatures, the selected values are compared to the boiling point temperatures taken from assessed vapour pressure curves presented in chapter 6.2.

Main emphasis has been given to the assessment of the critical point data where only a few direct measurements compare to a large number of predicted values (Ref. 1, chapter 2.5.1). The main experimental methods for measurements in the critical region are described. For lithium no measurements in the critical region are available. The various estimates of the critical temperature differ by over a thousand degrees and range from 3000 to 4400 K (Ref. 1, chapter 2.5.1). For sodium, only recently was a second set of measurements in the critical region reported (Ref. 9). Uncertainties on the exact location of the critical point still remain for potassium (Refs. 8, 10, 11), rubidium (Refs. 8, 12-16) and cesium (Refs. 8, 12, 15-24). In particular, recent improvements in density measurement indicate a critical temperature for Cs lower than the published values (Ref. 25).

* Chapter 6.1 of the IUPAC Handbook of Thermodynamic and Transport Properties of Alkali Metals, Editor R.W. Ohse, Blackwell Scientific Publications, Oxford 1985. Sections and chapters quoted in this paper refer to the Handbook.

EXPERIMENTAL METHODS

A survey of experimental techniques for measuring the critical constants has previously been prepared on behalf of IUPAC (Ref. 1). A brief review is given below.

Two methods of heat generation, static, described here, and dynamic (Ref. 26), have been used to achieve the required temperatures. The static techniques, using resistance heating inside cooled walls of a high-pressure vessel (autoclave) are limited presently to about 2800 K and 1600 bar by the reduced strength of the sample containers (Ref. 9). Considerably higher temperatures and pressures have been reached by dynamic methods such as the shock compression technique (chapter 6.7.1), the exploding wire (isobaric resistive heating) technique (Refs. 27-29) and laser (Refs. 26, 30), electron (Ref. 31) and neutron (Ref. 32) pulse heating techniques.

Static heating techniques for density and PVT measurementsOverflow pycnometer

Gol'tsova (Ref. 33) measured the liquid density of alkali metals up to 1850 K using an overflow type pycnometer (Fig. 1). The density at a given temperature was determined by weighing the liquid in the overflow container.

Pycnometer with electric meniscus determination

Hensel and Franck (Ref. 34) measured the equation of state of mercury in the supercritical region with a pycnometer. The position of the meniscus of the liquid metal was determined by electric resistance measurement (Fig. 2). Argon was used as the pressure-transmitting medium inside an internally-heated autoclave.

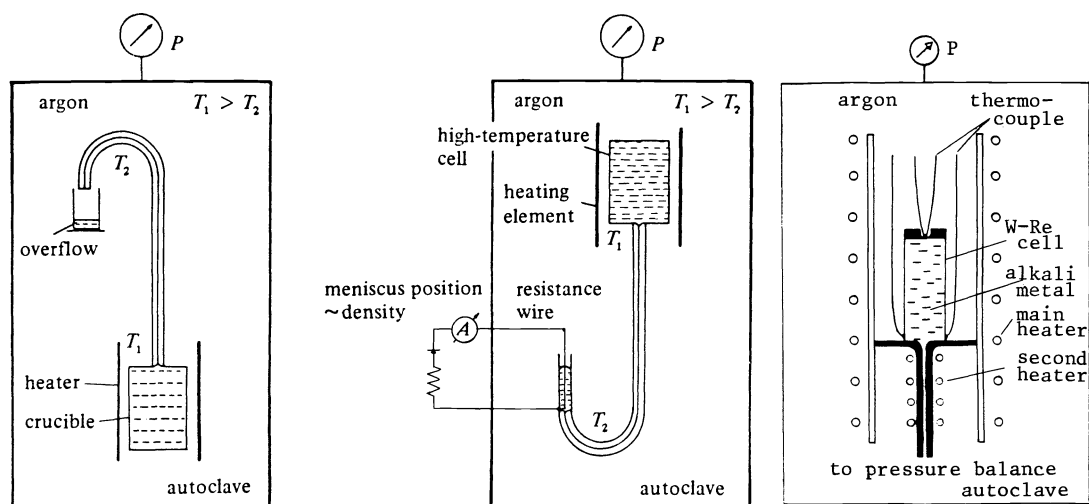


Fig. 1 Overflow pycnometer Fig. 2 Pycnometer with electric meniscus determination Fig. 3 Electrical conductivity cell pycnometer

Change in electrical conductivity

Renkert, Hensel, Franck and Freyland (Refs. 35, 36) used the drastic change in electrical conductivity caused by the onset of vaporization, i.e. the replacement of the liquid by the gas phase in the upper part of the cell to measure the saturation pressure. The pressure of the fluid metal within a thin W-Re cell was balanced by argon (Fig. 3). Four W-Re wires, fixed close to the top and bottom of the cell, were used for resistance (conventional potentiometry) and temperature (thermocouple) measurement.

Pycnometer with flexible bellows

Pfeifer et al. (Ref. 37) connected the high-temperature cell to a set of stainless steel bellows by a capillary of negligible volume, allowing simultaneous measurement of electric conductivity, Seebeck coefficient and density, in addition to temperature and pressure. The expansion of the bellows was measured by a closed mercury system using an inductive level indicator (Fig. 4.a).

A similar technique was used by Goldmann and Tödheide (Ref. 38) to determine the PVT-data of molten salts and by Hilber, Tödheide and Franck (Ref. 39) for measurements on aqueous salt solutions.

In a recent application to sodium at the JRC Karlsruhe (CEC), Binder (Ref. 9) replaced the closed mercury system by a displacement recorder using a linear differential transducer (Fig. 4.b).

Constant-volume pycnometer

Stone et al. (Ref. 40) used a constant-volume pycnometer (Fig. 5) with a thin metal membrane to measure the PVT-data of alkali metal vapours. The cell pressure was balanced by external gas pressure, an electric contact being used to control the membrane position for external gas-pressure regulation.

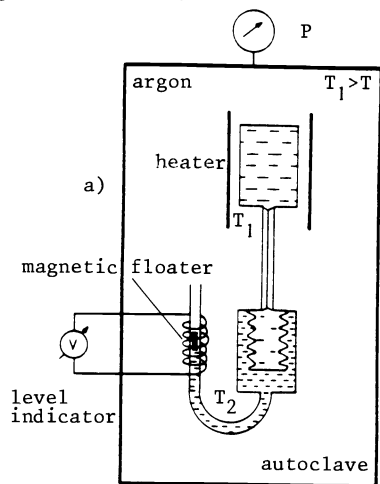


Fig. 4 Flexible-bellows pycnometer
a) mercury system with inductive level indicator
b) linear transducer

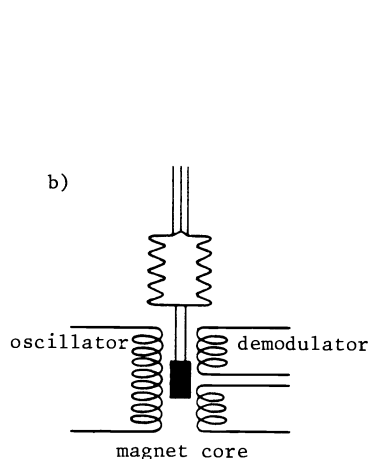
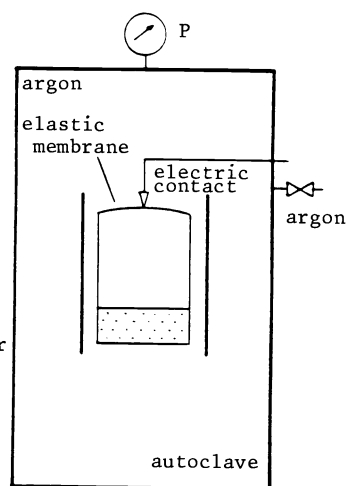


Fig. 5 Constant-volume pycnometer

Radiation-counting techniques - open system

Kikoin and Senchenkov (Ref. 41) determined the equation of state of mercury up to the temperature of 2300 K in the pressure range 200 - 5000 bar, using the intensity of γ -radiation from the ^{203}Hg isotope to measure the density of the fluid in a high-temperature cell. The pressure in the cell was controlled by the argon pressure inside a high-pressure autoclave, as shown schematically in Fig. 6.

Archimedean method

Postill et al. (Ref. 42) used an autoclave technique based on the Archimedean principle (Fig. 7). For isochoric measurements, constant density of the fluid was controlled by the buoyancy of a spherical sinker of known density. The position of the γ -active sinker was controlled by γ -detection. In order to follow an isochore, the pressure was adjusted during the temperature rise, such that the density of the fluid remained equal to that of the sinker and the position of the sinker remained unchanged.

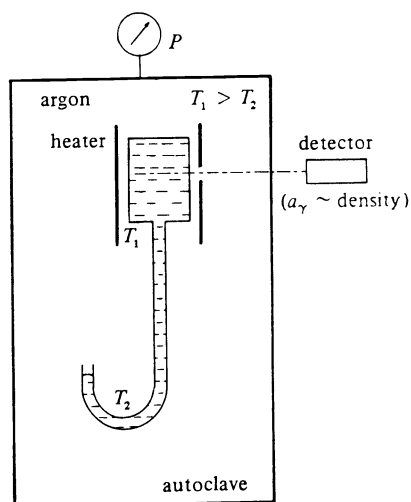


Fig. 6 Radiation-counting technique for density measurements-open system

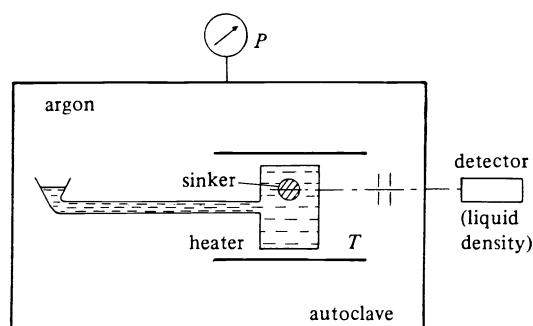


Fig. 7 Archimedean method for density measurements

Pressure-tube method

Silver and Bonilla (Ref. 20) developed the pressure-tube method (Fig. 8) for the determination of the vapour pressure of alkali metals up to 2500 K. The principal components are a closed-end pressure tube at high temperature, and a controllable liquid-oil injector at low temperature. The pressure of the oil injector system is plotted against the volume of the injected oil. The sharp break in the pressure curve, when the tube is just filled with liquid, indicates the vapour pressure at the temperature of the tube tip.

Tilting-capsule method

Oster and Bonilla (Ref. 18) developed the tilting-capsule method (Fig. 9) for determining the densities of the high-temperature saturated liquid and the vapour phases of alkali metals. The method relies on measuring the tilt angle of a cylindrical capsule, partially filled with the substance, as a function of temperature. The capsule is supported on transverse off-centre knife edges between two electric contacts indicating the position of the capsule within the furnace tube inside the pressure vessel (autoclave).

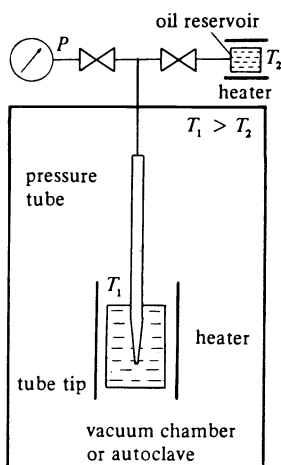


Fig. 8 Pressure-tube method

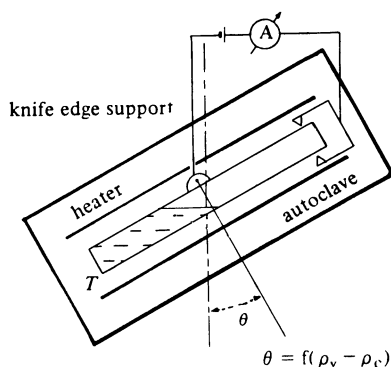


Fig. 9 Tilting-capsule method

Radiation-counting technique - sealed capsule

Dillon et al. (Ref. 12) developed a radiation-counting technique (Fig. 10) for the measurement of vapour and liquid densities of the alkali metals with the use of radioactive isotopes. A known quantity of alkali metal, sealed in a capsule, was irradiated in a thermal neutron flux to counting rates of reasonably short resolution times. Vapour- and liquid-density data near the critical temperature were analysed using the law of rectilinear diameter (Ref. 44), and the correlations suggested by Rowlinson (Ref. 43a) and Kordes (Ref. 43b).

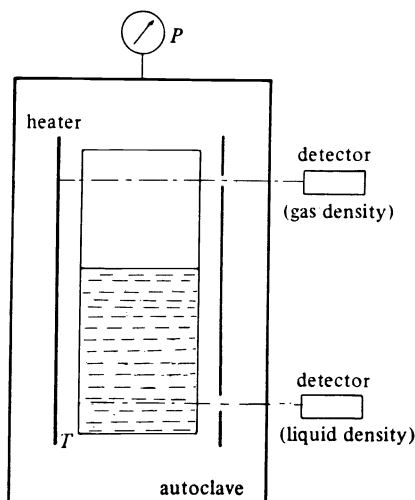


Fig. 10 Radiation-counting technique using a sealed specimen container for measurements along the coexistence curve

MELTING AND BOILING POINT

The melting and boiling temperatures of the alkali metals have been reviewed many times (Lyon, 1954, Ref. 45, Evans et al., 1955, Ref. 46, Gmelin, 1965, Ref. 47, Hultgren et al., 1973, Ref. 48, Vargaftik, 1975, Ref. 49, Foust, 1979, Ref. 50).

For the melting temperature, agreement was obtained with only few exceptions within one degree or less. Only in a few cases improvements were possible due to lower impurity contents achieved by refined purification techniques (see chapter 4.1 of this handbook).

Table 1 summarizes in chronological order the measured data and error limits, the experimental methods, purity content of the sample, and references. The selected values were taken from the average of experimental data after accounting for impurity content and error limits. Systematic errors are usually difficult to assess. Results with large deviations from the bulk of measured data were analysed and in case of inaccurate techniques and large impurity contents discarded before taking the average.

For the pressure dependence of the melting temperature reference is made to chapter 5.2, and the review of melting curves by Luedemann and Kennedy (Ref. 51).

Table 2 summarizes the measured boiling temperatures and error limits, the experimental methods and authors. The selected values agree well with the boiling temperatures obtained in chapter 6.2 from an assessment of all currently available experimental vapour pressure data. The values are close to the average of previous assessments by Lyon (Ref. 45), Foust (Ref. 50), Hultgren et al. (Ref. 48), Vargaftik (Ref. 49) and Shpil'rain (Ref. 52).

CRITICAL POINT DATA

Table 3 summarizes the measured and revised critical temperature, pressure and density data, and critical compressibility factor of sodium, potassium, rubidium and cesium.

In order to distinguish from the extrapolated data, the quantities measured directly are underlined. The predicted values are given in brackets. The data reported in the literature are discussed with special attention to the experimental and theoretical methods involved. Since there are no measurements available on the critical point data of lithium a new estimate is given applying the rules and relationships described in chapter 2.5.1.

Lithium

There are no measurements of the critical constants of Li. Estimates of the critical temperature differ by well over 1000 K and range from 3000-4400 K (Ref. 1, chapter 2.5.1). The main procedures for estimating the critical constants have been reviewed in chapter 2.5.1 and tested on Cs, Rb, K and Na for which measurements are available. The higher estimates of the critical temperature (3800-4450 K) are mainly obtained from the assumption of corresponding states behaviour of a vapour phase property such as the entropy of vaporization, vapour density (Kordes plot) and saturation vapour pressure. The lower estimates (\sim 3000 K) are obtained from the empirical Gates and Thodos correlation and the original van der Waals equation of state. Most estimation procedures, however, must be rejected on the grounds that they do not lead to reasonable values of the critical temperatures for Cs, Rb, K, and Na, for which measurements are now available (see chapter 2.5.1). The most accurate estimates of the critical temperatures of Cs, Rb, K, and Na, are obtained from a) the modified Guldberg rule and b) corresponding states behaviour of the reduced rectilinear diameter.

In the modified Guldberg rule the ratio T_b/T_c has been determined for Cs, Rb, K, and Na using the selected values of T_b given in table 2 and the measured critical temperatures given in table 3 and leads to $T_b/T_c = 0.4605$. The critical temperatures estimated using this relation are all within 2% of the measured values. Application of this result to Li yields $T_c = 3503 \pm 10$ K. Extrapolation of the averaged vapour pressure equation given in chapter 6.2 to this temperature leads to a critical pressure $P_c = 38.42 \pm 0.54$ MPa. A least squares analysis of the density data of Li assessed by Shpil'rain et al. (chapter 6.3.3) leads to the rectilinear diameter relation

$$\bar{\rho} = 280.2 - 4.847 \times 10^{-2} T \quad (800-2000 \text{ K}) \quad (1)$$

Extrapolation of the rectilinear diameter to the critical temperature yields a critical density $\rho_c = 110.4 \pm 0.5 \text{ kgm}^{-3}$.

TABLE 1 Measured and selected melting temperatures of the alkali metals

T _{mp} ,K	Error	Method	Sample Purity	Authors	Year	Ref.
<u>Lithium</u>						
452.2		Thermal Analysis		Zukowsky	1911	53
453.3	± 0.1	Thermal Analysis		Losana	1935	54
452.2		Cal. heat cont. meas.	99.5	Kilner	1952	55
453.69		Cal. heat cont. meas.	99.8	Douglas et al.	1955	56
453.6	± 0.5	Thermal Analysis	99.9	Keller et al.	1958	57
455	± 1.5	Thermal Analysis	99.8	Ponyatovskii	1961	58
454.9		Thermal Analysis		Weatherford et al.	1963	59
453.69	± 2.0	Diff. Thermal. Analysis	99.9	Luedemann et al.	1968	51
453.64	± 0.02	Thermal Analysis		Hubberstey et al.	1976	60
453.64	± 0.1	selected value				
<u>Sodium</u>						
371.05	± 0.05	Ice calorimeter	99.96	Rengade	1914	61
370.76		Cooling curve method		Griffiths	1914	62
370.78		Thermal Analysis		Bridgman	1914	63
370.85	± 0.05	Thermal Analysis		Edmonson et al.	1927	64
370.95	± 0.1	Thermal Analysis		Ladenburg et al.	1930	65
370.96	± 0.03	Ice calorimeter		Ginnings et al.	1950	66
370.65		Thermal Analysis	99.9	Ponytovskii	1961	58
370.018	± 0.005	Adiab. calorimeter		Martin	1967	67
371.05		Cooling Technique		Anderson et al.	1970	68
370.75		Thermal Analysis	99.9	Mirwald et al.	1976	69
370.95	± 0.1	Sound velocity meas.	99.9	Kamioka	1982	70
370.90	± 0.1	selected value				
<u>Potassium</u>						
336.65	± 0.05	Ice calorimeter	99.96	Rengade	1914	61
336.80	± 0.05	Thermal Analysis		Edmonson et al.	1927	64
336.56		Nernst type calorimeter	99.9	Carpenter et al.	1939	71
336.35	± 0.5	Heat content meas.		Douglas et al.	1952	72
336.15		Thermal Analysis		Grachev	1960	73
336.45	± 0.2	Density measurement	98.5	Basin et al.	1969	74
336.86		Cooling technique		Ott et al.	1970	75
336.55	± 0.2	selected value				
<u>Rubidium</u>						
312.15	± 0.05	Ice calorimeter	99.96	Rengade	1914	61
311.90	± 0.5	Thermal Analysis	99.6	Dauphinee et al.	1955	76
312.54		Cooling curve method		Weatherford	1963	59
312.65	± 0.01	Cal. spec. heat meas.		Filby et al.	1965	77
312.31	± 0.05	Density measurement	99.98	Basin et al.	1969	74
312.45		Thermal Analysis		Ott et al.	1970	75
312.47		Adiab. calorimeter	99.9	Martin	1970	78
312.65	± 0.1	selected value				
<u>Cesium</u>						
301.60	± 0.05	Ice calorimeter	99.96	Rengade	1914	61
301.75		Thermal Analysis		De Boer et al.	1930	79
301.45		Thermal Analysis		Rinck	1934	80
301.95	± 0.1	Thermal Analysis		Losana	1935	54
301.75		Ion current method		Taylor et al.	1937	81
301.79	± 0.17	Ice calorimeter		Clusius et al.	1954	82
302.15		Diff. Thermal Analysis		Kennedy et al.	1962	83
301.55	± 0.01	Cal. spec. heat meas.		Filby et al.	1965	77
301.65	± 0.2	Density measurement	99	Basin et al.	1969	74
301.67	± 0.13	Adiab. calorimeter	99.9	Martin	1970	78
301.59	± 1.0	Thermal Analysis		Ott et al.	1970	75
301.60	± 0.05	selected value				

TABLE 2 Measured boiling temperatures of the alkali metals

T_{bp}, K	Error	Method	Authors	Year	Ref.
<u>Lithium</u>					
1613		Vapour pressure measurement	Bohdansky et al.	1965/67	3
1615.6	± 1.0	Static equil. method	Anisimov, Volyak	1969	5
1613.56		Heat-pipe B.P. method	Schins et al.	1971	6
1608.2		Vapour pressure measurement	Rajagopalan, Bonilla	1981	7
1613	± 2.0	selected value			
<u>Sodium</u>					
1156		Vapour pressure measurement	Heycook et al.	1912	84
1156		Vapour pressure measurement	Ladenburg et al.	1930	65
1154.5	± 4.7	Vapour pressure measurement	Makansi et al.	1955	85
1154.52		Vapour pressure measurement	Bonilla et al.	1962	86
1156		Vapour pressure measurement	Sowa	1963	87
1154.59		Vapour pressure measurement	Bowles et al.	1965	88
1150.15		Vapour pressure measurement	Achener et al.	1966	89
1154.6	± 4.3	Vapour pressure measurement	Stone et al.	1966	40
1156.0		Static equilibr. method	Vinogradov et al.	1966	90
1154.4		Vapour pressure measurement	Fischer	1966	91
1156		Vapour pressure measurement	Bohdansky et al.	1967	3
1155.5		Vapour pressure measurement	Achener et al.	1967	92
1155.12		Heat-pipe B.P. method	Schins et al.	1971	6
1155.2		Pressure tube method	Bhise-Bonilla	1977	8
1154.6		Vapour pressure measurement	Das Gupta, thesis	1977	93
1154.5	± 1.0	selected value			
<u>Potassium</u>					
1030.5		Thermal Analysis	Ruff-Johannson	1905	100
1027		Vapour pressure measurement	Makansi et al.	1956	85
1034		Boiling point technique	Walling	1963	106
1032.13		Vapour pressure measurement	Achener	1967	92
1034.0		Static equilibr. method	Vinogradov et al.	1966	90
1029.8		Vapour pressure measurement	Stone et al.	1966	40
1029.39		Constant volume piezometer	Shpil'rain et al.	1968	107
1029.3	± 1.2	Boiling point technique	Shpil'rain, Nikanov	1971	105
1033.06		Heat-pipe B.P. method	Schins et al.	1971	6
		Vapour pressure measurement	Cherneeva et al.	1972	95
			Belova et al.	1980	97
1031	± 1.0	selected value			
<u>Rubidium</u>					
969	± 5.0	Thermal Analysis	Ruff-Johannson	1905	100
958.88		Vapour pressure measurement	Bonilla et al.	1962	86
958.7		Thermal Analysis	Weatherford et al.	1963	59
963.35		Vapour pressure measurement	Achener et al.	1964	98
962		Vapour pressure measurement	Bohdansky et al.	1967	3
960.1	± 0.3	Static equilibr. method	Volyak et al.	1968	99
961.21		Heat-pipe B.P. method	Schins et al.	1971	6
958		Boiling point technique	Shpil'rain, Nikanov	1971	105
960.23		Vapour pressure measurement	Cherneeva et al.	1972	96
960	± 1.0	selected value			
<u>Cesium</u>					
943	± 5.0	Thermal Analysis	Ruff-Johannson	1905	100
976.2	± 0.1	Positive-ion method	Taylor et al.	1937	81
939.40		Vapour pressure measurement	Bonilla et al.	1962	86
942.35(944.85)		Vapour pressure measurement	Achener	1964/68	98/102
942.04		P.V.T. measurement	Ewing et al.	1966	103
942		Vapour pressure measurement	Stone et al.	1966	40
939		Vapour pressure measurement	Bohdansky	1965/67	3
941.7		Vapour pressure measurement	Shpil'rain, Belova	1967	104
942.19		Heat-pipe B.P. method	Schins et al.	1971	6
941.5		Vapour pressure measurement	Cherneeva, Proskurin	1972	96
942.02		Boiling point method	Shpil'rain, Nikanorov	1972	105
941.5	± 1.0	selected value			

TABLE 3 Measured and revised critical point data of sodium, potassium, rubidium and cesium

T_c, K	P_c, MPa	$\rho_c, kg \cdot m^{-3}$	z_c	year authors	method	Ref.
<u>Sodium</u>						
2503.3	<u>25.64</u>			1976 Bhise, thesis	Pressure tube method	8.a
2503.3	<u>25.64</u>			1977 Bhise, Bonilla	Rev. of exp. data	8,b
2508.7±12.5	<u>25.64</u> ±0.02	(214,1±0,9)		1977 Das Gupta, thesis	Rev. of exp. data	93
<u>2485 ±15</u>	<u>24.8</u> ±0.5	300 ±50		1984 Binder, Franck	Flexible-bellow pycnometer with linear transducer	9
<u>Potassium</u>						
<u>2198 ±30</u>	<u>15.5</u> ±1.5			1972 Freyland, Hensel	Change in electr. cond.	10
2280.8±3	<u>16.39</u> ±0.03			1973 Jerez et al.	Pressure tube method	11
2280.8	<u>16.39</u>	(188.1)		1977 Bhise, Bonilla	Rev. of exp. data	8
<u>Rubidium</u>						
2093 ±35		346 ±9		1966 Dillon et al.	Density by rad. count.	12
2106 ±6		<u>347 ±2</u>		1973 Chung, Bonilla	Tilting-capsule method	13
2106 ±5	<u>13.39</u> ±0.02			1973 Bhise, Bonilla	Pressure tube method	14
2105.9	<u>13.39</u>	347	0.188	1977 Bhise, Bonilla	Rev. of exp. data	8
<u>2093 ±20</u>	<u>14.5</u> ±0.1	320 ±20	0.22	1980 Franz, thesis, 1980 Franz et al.	Change in electr. cond.	15 16
<u>Cesium</u>						
2027.6	(13.25)	451		1965 Hochman, Bonilla	Voltage drop method	17
2057 ±40	(14.7)	428 ±12		1966 Dillon et al.	Density by rad. count.	12
<u>2048</u>		<u>407</u>		1967 Oster, thesis	Tilting capsule method	18a
2052.3±2	<u>11.75</u> ±0.04			1968 Silver, thesis	Pressure tube method	19
2050.9±2	<u>11.71</u> ±0.04			1970 Silver, Bonilla	Rev. of exp. data	20
<u>2050</u>		406		1970 Oster, Bonilla	Rev. of exp. data	18b
2033 ±20	11.65±0.5	400 ±20	0.23	1970 Alekseev et al.	Radiation counting	21
<u>2023 ±30</u>	<u>11.0</u> ±1			1971 Renkert et al.	Change in electr. cond.	22
2051 ±4	11.73±0.04	420		1973 Das Gupta et al.	Rev. of exp. data	23
2043 ±20	12.16±1	440 ±50	0.216	1975 Korshunov et al.	Radiation counting	24
2051.2	11.73	420	0.217	1977 Bhise, Bonilla	Rev. of exp. data	8
<u>2013 ±20</u>	<u>11.35</u> ±0.1	410 ±20	0.22	1980 Franz, thesis, 1980 Franz, et al.	Change in electr. cond. and PVT mea.	15 16

directly measured data underlined
 predicted values in brackets

In chapter 2.5.1 it has been shown using the low temperature ($T_r \lesssim 0.5$) density data that the alkali metals show corresponding states behaviour provided one uses a different set of scaling temperatures for the liquid and vapour phases. The scaling temperatures found for the liquid alkali metals are very close to the measured values of T_c for Cs, Rb, K, Na, whereas those found for the vapour phase are considerably higher. It follows that previous applications of corresponding states behaviour which use vapour phase properties do not yield the correct critical temperatures. A correct application of corresponding states theory to estimate the critical temperatures of the alkali metals requires scaling of a liquid phase property. In particular, corresponding states theory requires that the slope of the reduced rectilinear diameter, i.e., BT_c/ρ_c , has a universal value. The low-temperature rectilinear diameter $\bar{\rho} = A-BT$, is determined essentially by the liquid density (in contrast to the Kordes plot, which is determined essentially by the vapour density) and can be regarded as a liquid phase property. For cesium, using the value of B from Equ. 5, the average value of T_c from Table 3, and the value of ρ_c obtained from the extrapolated rectilinear diameter to this temperature, the slope of the reduced rectilinear diameter has the value $BT_c/\rho_c = 1.372 \pm 0.041$ where the uncertainty has been determined from the scatter in the value of T_c . The values of the critical temperatures and densities of Rb, K, Na and Li may be obtained directly by extrapolating the rectilinear diameters to the critical point and using the result $BT_c/\rho_c = 1.372$. The critical temperatures thus obtained for Rb, K, Na are within 2 % of the measured values given in table 3. For Li the procedure leads to the values $T_c = 3344 \pm 42$ K, $\rho_c = 118 \pm 2$ kgm⁻³. Extrapolation of the averaged vapour pressure equation given in chapter 6.2 to this temperature gives $P_c = 30.4 \pm 2.0$ MPa. estimated critical temperatures differ by approximately 150 K and this results in 8 MPa difference in the estimated critical pressure. It is not possible to determine which estimated critical temperature is the more reliable although the value obtained from corresponding states behaviour has a more sound theoretical foundation. The recent estimate of Rajagapalan and Bonilla of $T_c = 3494$ K is close to the value 3503 K in table 4 as is to be expected since both estimates are based on the modified Guldberg rule. The critical temperatures given in table 4 are considerably lower than the estimated value of Shpil'rain et al. (chapter 6.3.3) of $T_c = 3680$ K.

TABLE 4 Best estimates of the critical constants of Li

Procedure	T_c	P_c (MPa)	ρ_c (kgm ⁻³)
Empirical relations (Modified Guldberg rule, law of rectilinear diameter, extrapolation of vapour pressure equation)	3503±10	38.42±0.54	110.4±0.5
Corresponding states behaviour of the liquid densities	3344±42	30.4±2.0	118±2

Sodium

Two sets of measurements are available of the critical point determination of sodium (Refs. 8, 9). Bhise and Bonilla (Ref. 8) used the pressure tube method (Fig. 8), which gives direct access to the critical pressure, and obtained a critical pressure $P_c = 25.64 \pm 0.02$ MPa. The critical temperature, $T_c = 2503.3$ K, was obtained by extrapolating the measured vapour pressure curve to this pressure. Das Gupta (Ref. 93) re-analysed the Bhise and Bonilla vapour pressure data (Ref. 8). A least square analysis of the vapour pressure data, including the data of Stone et al. (Ref. 40a), led to a revised critical temperature of $T_c = 2508.7$ K. Recently, Binder (Ref. 9), using a flexible bellow technique with a linear transducer (Fig. 4b), reported direct PVT measurements in the critical region. The critical point was located from the break in the isotherm at the saturation vapour line (two phase envelope). The critical constants were estimated to be $T_c = 2485 \pm 15$ K, $P_c = 25.5 \pm 0.5$ MPa, and $\rho_c = 300 \pm 50$ kgm⁻³. The critical temperature and pressure are in good agreement with the values reported by Bhise and Bonilla but the critical density is about 50 % higher than the estimated values discussed in chapter (2.5.1). This discrepancy can only be clarified by further experiments. Recently,

Petiot and Seiler (94) have reported vapour pressure measurements up to 2250 K and vapour density measurements at the three temperatures 1960, 2130, and 2280 K. The authors estimated a critical temperature of $T_c = 2630 \pm 50$ K from the Kordes plot using the vapour density data and liquid density data of Dillon et al. (12). A critical pressure of $P_c = 34 \pm 4$ MPa was obtained by extrapolation of the vapour pressure curve to this temperature. The critical density, $\rho_c = 205 \text{ kgm}^{-3}$, was obtained by a second extrapolation procedure proposed by Kordes.

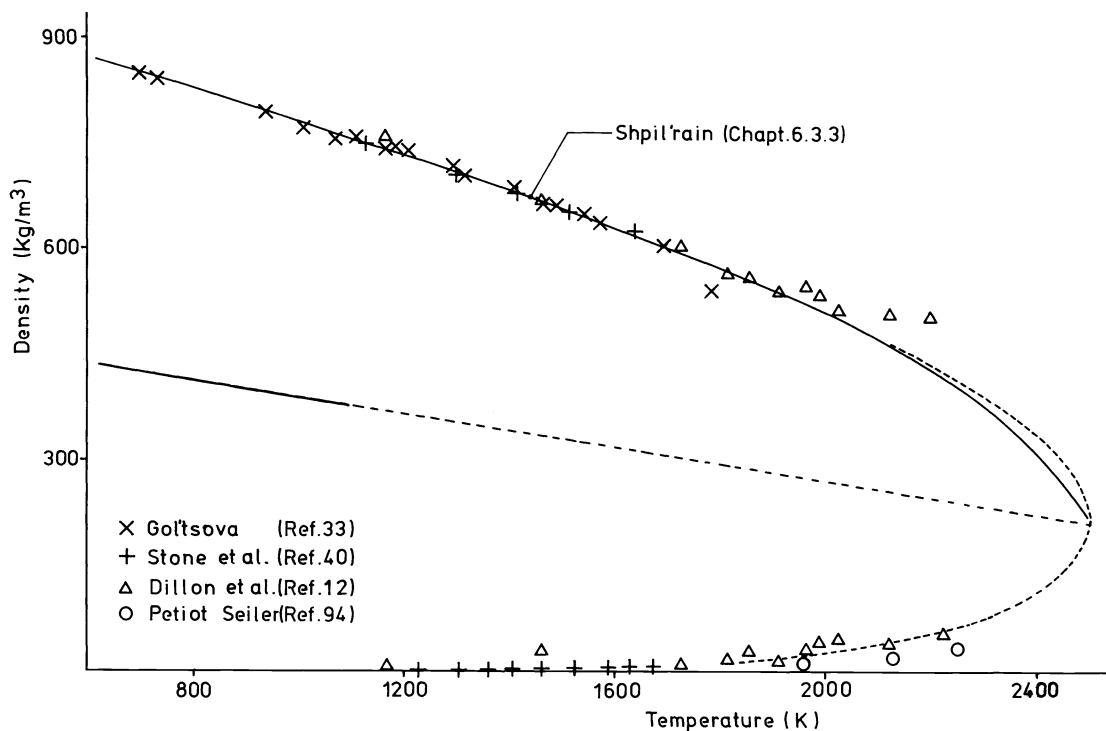


Fig. 11 Measured liquid and vapour density data of sodium (solid line: assessment of liquid density data by Shpil'rain et al. (chapter 6.3.3))

The measured liquid and vapour saturation densities are shown in fig. 11. The assessment of liquid density data (solid line) by Shpil'rain et al. (chapter 6.3.3) is based on the data of Gol'tsova (Ref. 33), Stone et al. (Ref. 40a), Ewing et al. (Ref. 40b), and Dillon et al. (Ref. 12). The rectilinear diameter was evaluated using the accurate low-temperature (400-1300 K) density data given by Shpil'rain (chapter 6.3.3) and led to the relation

$$\bar{\rho} \text{ (kgm}^{-3}\text{)} = 508.8 - 1.1929 \times 10^{-1} T(\text{K}) \quad (400\text{-}1300 \text{ K}). \quad (2)$$

Taking a critical temperature of $T_c = 2497$ K, the average of the measured values given by Das Gupta and Binder, leads to a critical density $\rho_c = 211 \text{ kgm}^{-3}$ from the extrapolated rectilinear diameter. The dashed curves shown in Fig. 11 represents a reasonable description of the variation of the vapour and liquid densities in the critical region consistent with the critical coordinates found above and the rectilinear diameter.

Potassium

Two sets of measurements are available on the critical point determination of potassium (Refs. 10, 11). Freyland and Hensel (Ref. 10) determined the critical pressure and temperature from the steepest drop in electrical resistance and thermoelectric power (Fig. 3) and reported the values $T_c = 2198 \pm 30$ K and $P_c = 15.5 \pm 1.5$ MPa, respectively. Jerez et al. (Ref. 11), using the pressure tube method, measured a critical pressure $P_c = 16.39 \pm 0.03$ MPa and obtained a critical temperature $T_c = 2280.8 \pm 3$ K from the extrapolated vapour pressure curve.

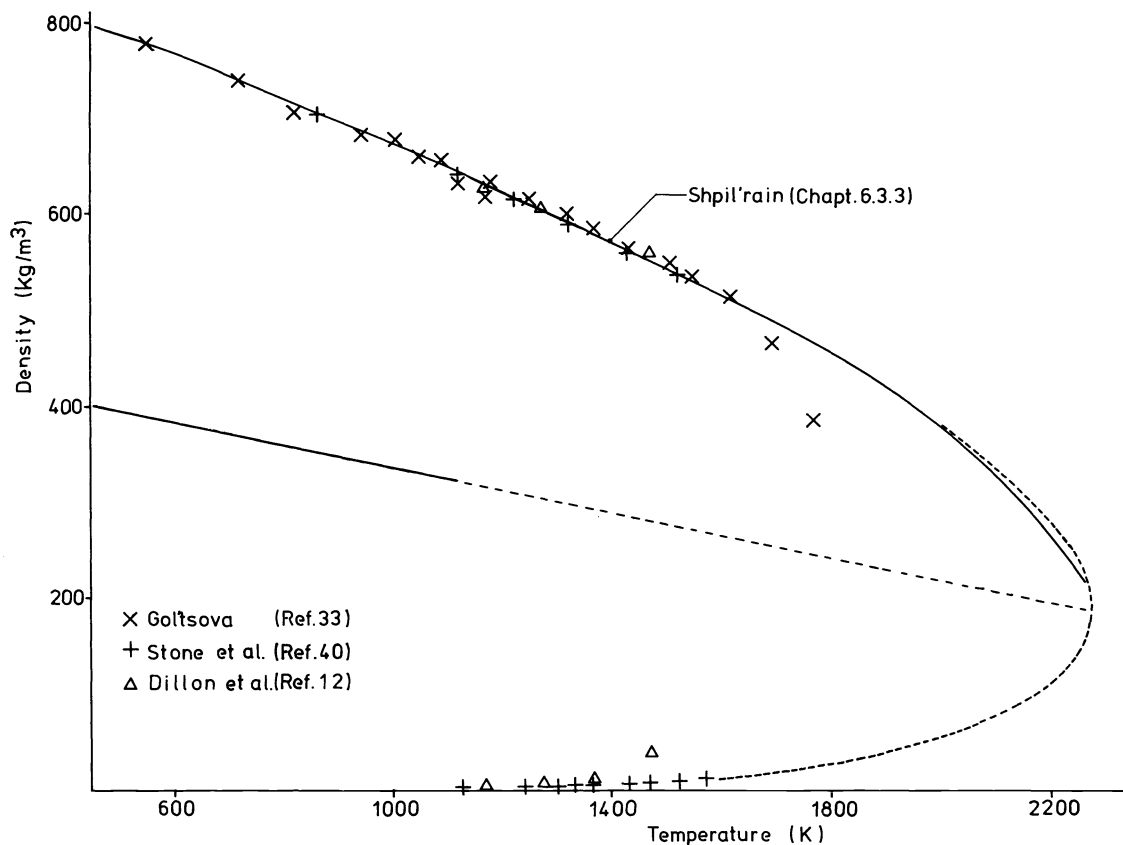


Fig. 12 Measured liquid and vapour density data of potassium (solid line: assessment of liquid density data by Shpil'rain et al. (chapter 6.3.3))

The measured liquid and vapour densities are shown in Fig. 12. The assessment of the liquid density data (solid line) by Shpil'rain et al. (chapter 6.3) is based on the data of Gol'tsova (33), Stone et al. (40), and Dillon et al. (12). The rectilinear diameter was evaluated using the more accurate low-temperature (400-1150 K) density data assessed by Shpil'rain (chapter 6.3.3) and led to the relation

$$\bar{\rho} \text{ (kgm}^{-3}\text{)} = 454.2 - 1.1732 \times 10^{-1} T(\text{K}) \quad (400-1150 \text{ K}) \quad (3)$$

Using a critical temperature of $T_c = 2239 \text{ K}$ leads to a critical density of $\rho_c = 192 \text{ kgm}^{-3}$.

The dashed curves shown in Fig. 12 represents a reasonable description of the variation of the vapour and liquid densities in the critical region, consistent with the critical coordinates given above and the extrapolated rectilinear diameter.

Rubidium

For rubidium four sets of high-temperature PVT measurements in the critical region using different techniques are available. Dillon et al. (Ref. 12) measured the saturation vapour and liquid densities close to the critical temperature and, using the law of rectilinear diameter, the Kordes plot, and the correlation of Rowlinson, estimated a critical temperature and density of $T_c = 2093 \pm 35 \text{ K}$ and $\rho_c = 346 \pm 9 \text{ kgm}^{-3}$ respectively. Chung and Bonilla (Ref. 13), using the tilting capsule method (Fig. 9), measured a critical temperature $T_c = 2106 \pm 6 \text{ K}$ and critical density $\rho_c = 347 \pm 2 \text{ kgm}^{-3}$. Bhise and Bonilla (Ref. 8b), using the pressure tube method,

measured a critical pressure $P_c = 13.39 \pm 0.02$ MPa and determined a critical temperature of $T_c = 2106 \pm 5$ K by extrapolation of the vapour pressure curve to this pressure. Franz et al. (Refs. 15, 16) determined the critical temperature, pressure, and density from the steepest drop in density and electrical conductivity as a function of pressure at constant temperature (Fig. 3) to be $T_c = 2093 \pm 20$ K, $P_c = 14.5 \pm 0.1$ MPa, and $\rho_c = 320 \pm 20$ kgm⁻³, respectively.

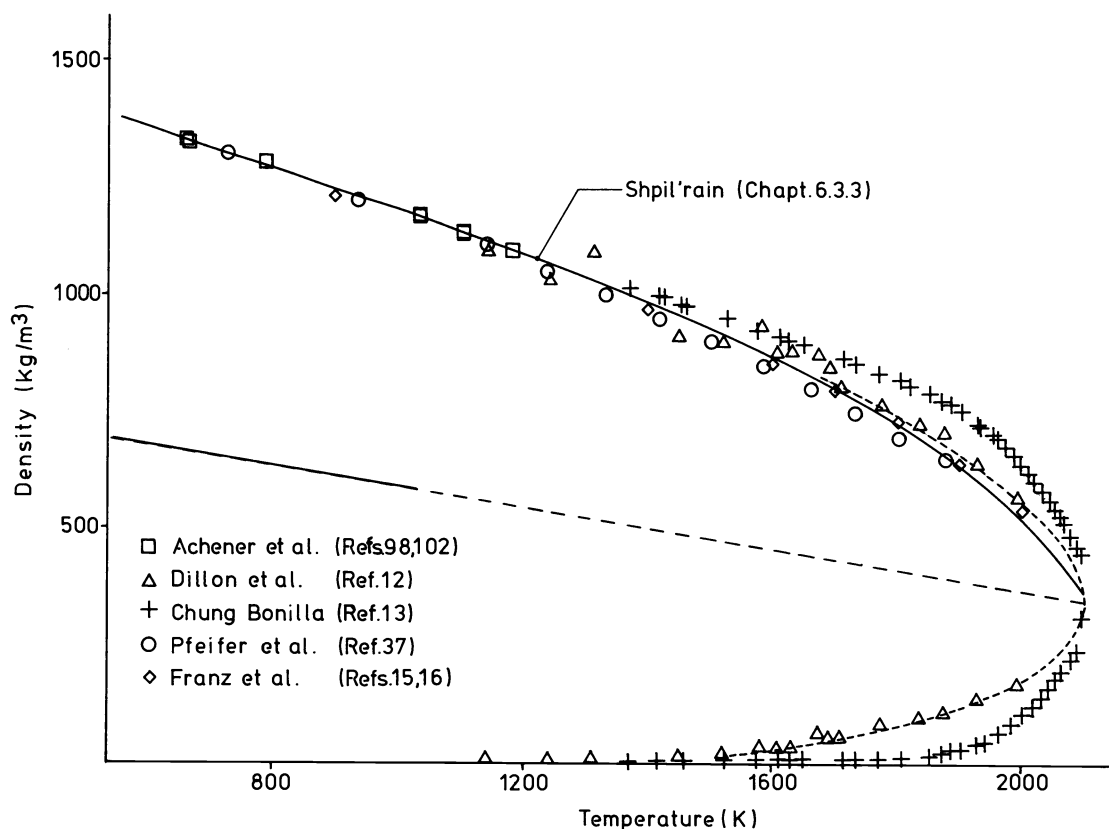


Fig. 13 Measured liquid and vapour density data of rubidium (solid line: assessment of liquid density data by Shpil'rain et al. (chapter 6.3.3))

The measured liquid and vapour saturation densities are shown in Fig. 13. For the liquid densities, there is a good agreement between the data of Dillon et al. (Ref. 12), Achener et al. (Refs. 98, 102), Pfeifer et al. (Ref. 37), and Franz et al. (Ref. 16), whereas the data of Chung and Bonilla (Ref. 13) deviate beyond 1400 K. The assessment of the liquid density data (solid line) by Shpil'rain et al. (chapter 6.3.3) is based on the data of Dillon et al., Achener et al., Pfeifer et al., and Franz et al. The rectilinear diameter obtained using the more accurate low-temperature (400-1050 K) data given by Shpil'rain et al. (chapter 6.3.3) is given by relation

$$\bar{\rho} \text{ (kgm}^{-3}\text{)} = 813.1 - 2.2140 \times 10^{-1} T(\text{K}) \quad (400-1050) \text{ K} \quad (4)$$

Taking a critical temperature of 2100 K, the average of the measured values given by Chung, Bhise and Bonilla, and Franz et al., leads to a critical density of $\rho_c = 348$ kgm⁻³. The dashed curves shown in Fig. 13 represent a reasonable description of the vapour and liquid densities in the critical region consistent with the critical coordinates obtained above and the extrapolated rectilinear diameter.

Cesium

For cesium eight sets of high temperature PVT measurements in the critical region using five

different techniques are available. Hochman and Bonilla (Ref. 17) measured the volume of the liquid and vapour phases by locating the liquid meniscus level from the voltage drop in a vertical tube. They estimated a critical temperature $T_c = 2027.6$ K, critical density $\rho_c = 451$ kgm^{-3} , critical pressure $P_c = 13.25$ MPa (by extrapolating vapour pressure curve of Bonilla et al. (Ref. 86) to T_c). Dillon et al. (Ref. 12) measured the liquid and vapour densities close to the critical point using the radiation counting technique (Fig. 10) and estimated the critical constants to be $T_c = 2057 \pm 40$ K, $\rho_c = 428 \pm 12$ kgm^{-3} , and $P_c = 14.7$ MPa (by extrapolating the vapour pressure curve of Bonilla et al. to T_c). Oster and Bonilla (Ref. 18), using the tilting capsule method (Fig. 9), obtained $T_c = 2048$ K and $\rho_c = 407$ kgm^{-3} . Silver (Ref. 19), using the pressure tube method, obtained a critical pressure $P_c = 11.75 \pm 0.04$ MPa and a critical temperature $T_c = 2052.3$ K by extrapolation of the vapour pressure curve. Silver and Bonilla (Ref. 20) reported the values $T_c = 2050.9$ K and $P_c = 11.71$ MPa as an average between the values reported by Oster (Ref. 18) and Silver (Ref. 19). Alekseev et al. (Ref. 21), using a radiation counting technique (Fig. 10), determined the critical constants $T_c = 2033 \pm 20$ K, $P_c = 11.65 \pm 0.5$ MPa, and $\rho_c = 400 \pm 20$ kgm^{-3} . Korshunov et al. (Ref. 24), using a γ -counting technique, obtained $T_c = 2043 \pm 20$ K, $P_c = 12.16 \pm 1$ MPa, and $\rho_c = 440 \pm 50$ kgm^{-3} . Renkert et al. (Ref. 22), using the change in electrical resistivity (Fig. 3), obtained $T = 2023 \pm 30$ K, and $P_c = 11.0 \pm 1$ MPa. More recently, Franz et al. (Ref. 16) using the same technique obtained $T_c = 2013 \pm 20$ K and $P_c = 11.35 \pm 0.1$ MPa. Recent improvements on the accuracy of density measurements indicate that this critical temperature may still be too high (Ref. 25).

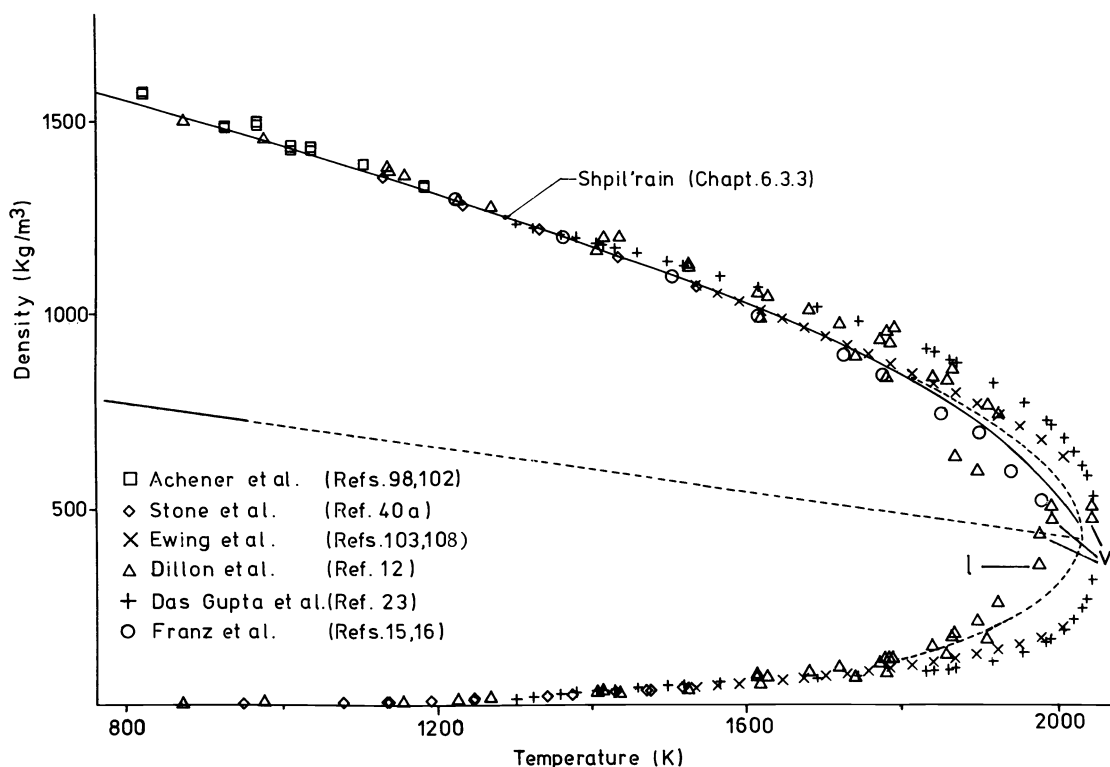


Fig. 14 Measured liquid and vapour density data of cesium (solid line: assessment of liquid density data by Shpil'rain et al. (chapter 6.3.3))

The measured liquid and vapour saturation densities are shown in Fig. 14. The assessment of the liquid density data (solid line) by Shpil'rain et al. (chapter 6.3.3) follows the data of Achener et al. (Refs. 98, 102), Franz et al. (Refs. 15, 16), Stone et al. (Ref. 40a), Ewing et al. (Refs. 103, 108) and Dillon et al. (Ref. 12). The data of Das Gupta et al. (Ref. 23) again show a systematic deviation from the bulk of all other data towards higher liquid and lower vapour densities as already observed for Rb. The rectilinear diameter was evaluated using the low-temperature (400-950 K) density data assessed by Shpil'rain (chapter 6.3.3)

and led to the relation

$$\bar{\rho} \text{ (kgm}^{-3}\text{)} = 1004 - 2.8472 \times 10^{-1} T(\text{K}) \quad (400-950) \quad (5)$$

Using a critical temperature of $T_c = 2035 \text{ K}$, an average of the measured values reported by Silver and Bonilla (Ref. 20), Renkert et al. (Ref. 22), Das Gupta et al. (Ref. 23), and Franz et al. (Ref. 16), leads to a critical density of $\rho_c = 425 \text{ kgm}^{-3}$ from the extrapolated rectilinear diameter. The dashed curve shown in Fig. 12 represents a reasonable description of the variation of the vapour and liquid densities in the critical region consistent with the critical coordinates $T_c = 2035 \text{ K}$, $\rho_c = 425 \text{ kgm}^{-3}$, the extrapolated rectilinear diameter and the high-temperature density data.

CONCLUSION

The measured and revised data of the melting, boiling and critical point temperature are reviewed.

Selected values are given for the melting and boiling point temperatures. Table 5 compares the selected values with previous assessments. The selected boiling point temperatures are in good agreement with the values obtained in chapter 6.2 from the assessment of vapour pressure measurements. Close agreement between the various assessments is observed for all alkali metals.

TABLE 5 Selected values of melting and boiling point temperatures compared to previous assessments

Source (Assessments)	Melting temperatures (K)					Boiling temperatures (K)				
	Li	Na	K	Rb	Cs	Li	Na	K	Rb	Cs
Shpil'rain (52) 1970	453.69	371.0	336.60	312.65	301.55	1611.6	1154.7	1029.9	958	940.7
Foust (50) 1972		370.97								
Hultgren et al. (48) 1973	453.7	371.0	336.35	312.64	301.55	1615	1156	1032	961	944
Vargaftik (49) 1975)1978	453.7	371.0	336.4	312.7	301.6	1615	1151.2	1032.2	959.2	943
Vapour press. assess- ment (chapt.6.2)						1612.1 ±4.7	1154.8 ±1.1	1030.7 ±5.2	959.8 ±2.4	941.6 ±0.9
Selected value	453.64 ±0.1	370.9 ±0.1	336.55 ±0.2	312.65 ±0.1	301.6 ±0.05	1613 ±2.0	1154.5 ±1.0	1031 ±1.0	960 ±1.0	941.5 ±1.0

Emphasis has been given to the assessment of the critical point data and the experimental techniques used for measurements in the critical region. For the selected values of temperature and pressure, given in Table 6, the averages ($1/T$, $\log p$) of the directly measured or revised data (Table 3) were taken. The critical densities were calculated from the rectilinear diameters (Eqs. 2-5) extrapolated to the selected critical temperatures. For comparison previous assessments are given. Reasonable agreement has been obtained except for the critical pressure of sodium where previous estimates are higher. The averaged temperatures for Cs, Rb, K and Na have been used to test the various estimation procedures discussed in chapter 2.5.1, and in the assessment of the saturation liquid and vapour densities in Figs. 11-14.

For Li, the estimate of the critical temperature from the modified Guldberg rule is in good agreement with recent values reported by Ragajopalan and Bonilla (Ref. 7). The estimated critical temperature based on corresponding states behaviour of the liquid densities is, however, considerably lower than the assessed values of Vargaftik (Ref. 49), Bonilla et al. (Ref. 7), and Shpil'rain et al. (chapter 6.3.3).

TABLE 6 Comparison of selected critical point data with previous assessments

References	T _c (K)	P _c (MPa)	ρ _c (kg/m ³)
<u>Lithium</u>			
Mod. Guldberg (chapt. 2.5.1)	3503 ±10	38.42±0.54	110.4±0.5
PCS (chapt. 2.5.1)	3344±42	30.4±2.0	118 ±2
Vargaftik (49)	3800	97	100
Rajagopalan et al. (7)	3494	37.78	
Shpil'rain et al. (chapt. 6.3.3)	3680		118
<u>Sodium</u>			
Das Gupta (93)	2508.7±12.5	25.64±0.02	(214.1±0.9)
Binder (9)	2485±15	24.8±0.5	(300±50)
selected value	2497±18	25.22±0.6	211±2
Achener et al. (102)	2573±60	34.15±4	206±16
Vargaftik (49)	2500	37	180
Shpil'rain et al. (chapt. 6.3.3)	2505		218
<u>Potassium</u>			
Freyland, Hensel (10)	2198±30	15.5±1.5	
Jerez et al. (11)	2280.8±3	16.39±0.03	
selected value	2239±49	15.95±0.6	192±6
Achener et al. (102)	2173±50	16.72±2.1	202±15
Vargaftik (49)	2250	16.0	160
Shpil'rain et al. (chapt. 6.3.3)	2280		194
<u>Rubidium</u>			
Chung, Bhise, Bonilla (13, 14)	2106±6	13.39±0.02	347±2
Franz et al. (15, 16)	2093±20	14.5±0.1	320±20
selected value	2100±15	13.95±0.8	348±3
Achener et al. (102)	2083±15	18.2±2	347±6
Vargaftik (49)	2100	16.0	350
Shpil'rain et al. (chapt. 6.3.3)	2106		347
<u>Cesium</u>			
Silver, Bonilla (19)	2051±2	11.75±0.04	
Renkert et al. (22)	2023±30	11.0±1	
Das Gupta et al. (23), Bhise et al. (8)	2051±4	11.73±0.04	420
Franz et al. (16)	2013±20	11.35±0.1	410±20
selected value	2035±23	11.46±0.4	425±7
Achener et al. (102)	2043±10	13.37±0.8	434±5
Vargaftik (49)	2050	11.7	430
Shpil'rain et al. (chapt. 6.3.3)	2043		430

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REFERENCES

1. R.W. Ohse, H. v. Tippelskirch, IUPAC-Review, High Temp.-High Press., 9, 367-385, (1977).
2. D.V. Rigney, S.M. Kapelner, R.E. Cleary, Report TIM - 844 (1965).
3. J. Bohdansky, H.E.J. Schins, J. Phys. Chem., 71, 215-217 (1967).
4. E.E. Shpil'rain, A.M. Belova, High Temperature, 6, 330-331 (1968).
5. V.M. Anisimov, L.D. Voljak, Teplofizika Vysokikh Temperatur, 7, 371 (1969), engl. translation, High Temp., 7, 340-341 (1969).
6. H.E.J. Schins, R.W.M. Van Wijk, B. Dorpema, Z. Metallkde., 62, 330-336 (1971).
7. A.S. Rajagopalan, C.F. Bonilla, Proc., 8th Sympos. Thermophys. Prop., Gaithersburg 1981, (Editor J.V. Sengers) ASME II, 431-336 (1982).
- 8a. V.S. Bhise, Thesis, Columbia University New York (1976).
- 8b. V.S. Bhise and C.F. Bonilla, Proceed. 7th Sympos. on Thermophysical Properties, Gaithersburg 1977, ASME 910-916.
9. H. Binder, Dissertation, Inst. für Physikalische Chemie, Universität Karlsruhe 1984, Ber. Bunsenges. Phys. Chem. in press.
10. W.F. Freyland, F. Hensel, Ber. Bunsenges. Phys. Chemie, 76, 16-19 (1972).
11. W.R. Jerez, V.S. Bhise, S. Das Gupta, C.F. Bonilla, Proc. 6th Symp. Thermophys. Prop., Atlanta 1973, ASME 353-361.
12. I.G. Dillon, P.A. Nelson, B.S. Swanson, J. Chem. Phys., 44, 4229-4238 (1966); Report ANL-7025 (TID-4500), (1965); Rev. Sci. Inst. 37, 614, (1966).
13. J.-W. Chung, C.F. Bonilla, Proc. 6th Symp. Thermophys. Prop., Atlanta 1973, ASME, pp. 397-403.
14. V.S. Bhise, C.F. Bonilla, Proc. 6th Sympos. Thermophys. Prop., Atlanta 1973, ASME, pp. 362-368.
15. G. Franz, Dissertation, Fachbereich Phys. Chemie, Philipps-Universität Marburg (1980).
16. G. Franz, W. Freyland, F. Hensel, LAM 4, Grenoble 1980, J. de Physique, Coll. C8, Supplément 8, 41, C8-70 (1980).
17. J.M. Hochman, C.F. Bonilla, Proc. 3rd Symp. Thermophys. Prop., Purdue Univ. 1965, ASME 122-130 (1965).
- 18a. G.F. Oster, Thesis, Eng. Sci. Dept. Columbia University, New York 1967
- 18b. G.F. Oster, C.F. Bonilla, Proc. 5th Symp. Thermophys. Prop., Boston 1970, ASME, 468-474 (1970).
19. I.L. Silver, Thesis, Eng. Sci. Dept. Columbia University. New York 1968.
20. I.L. Silver, C.F. Bonilla, Proc. 5th Symp. Thermophys. Prop., Boston 1970, ASME, 461-467 (1970).
- 21a. V.A. Alekseev, Tep. Vys. Temp., 6, No. 6, 961-965 (1968).
- 21b. V.A. Alekseev, V.G. Ovcharenko, Yu.F. Ryzhkov, A.P. Senchenkov, Pisma v zhurnal eksp. i teoret. fiziki, 12, 306-309 (1970).
22. H. Renkert, F. Hensel, E.U. Franck, Ber. Bunsenges. Phys. Chem., 75, 502-512 (1971).
23. S. Das Gupta, V. Bhise, D.W. Stuteville, J.-W. Chung, C.F. Bonilla, Proc. 6th Symp. Thermophys. Prop., Atlanta 1973, 387-396 (1973).
24. Yu.S. Korshunov, S.P. Vetchinin, A.P. Senchenkov, E.I. Asinovskii, Teplofizika Vysokikh Temperatur, 13, 517-524 (1975).
25. F. Hensel, private communication.

26. R.W. Ohse, J.-F. Babelot, A. Frezzotti, K.A. Long, J. Magill, High Temp. Sci., 13, 35-78, (1980).
27. A. Cezairliyan, A.P. Miller, High Temp. - High Press., 9, 319 (1977).
28. J.W. Shaner, G.R. Gathers, C. Minichino, High Temp. - High Press., 9, 331 (1977).
29. W. Seydel, W. Fucke, Z. Naturforsch., 32a, 994 (1977).
30. R.W. Ohse, J.-F. Babelot, C. Cercignani, J.-P. Hiernaut, M. Hoch, G.J. Hyland, J. Magill, J. Nucl. Mat., 130, in press (1985)
31. D.A. Benson, E.G. Bergeron, Proc. Symp. Thermodyn. Nucl. Mat., Jülich 1979, IAEA, Vienna, I, 93-114 (1980).
32. K.O. Reil, M.F. Young, T.R. Schmidt, Report SAND 78-1561 (1978), Sandia Laboratories, Albuquerque, New Mexico.
33. E.I. Gol'tsova, Teplofizika Vysokikh Temperatur, 4, 360-363 (1966), Engl. transl. High. Temp., 4, 348-351 (1966).
34. F. Hensel, E.U. Franck, Ber. Bunsenges. Phys. Chem., 70, 1154 - 1161 (1966).
35. H. Renkert, F. Hensel, E.U. Franck, Ber. Bunsenges. Phys. Chem., 75, 507-512 (1971).
36. W.F. Freyland, F. Hensel, Ber. Bunsenges. Phys. Chem., 76, 16-19 (1972).
37. H.P. Pfeifer, W. Freyland, F. Hensel, Ber. Bunsenges. Phys. Chem., 83, 204-211, (1979).
38. G. Goldmann, K. Tödheide, Z. Naturforsch. 31a, 656 (1976).
39. R. Hilbert, K. Tödheide, E.U. Franck, Ber. Bunsenges. Phys. Chem., 81, 1115 (1977).
- 40a. J.P. Stone, C.T. Ewing, J.R. Spann, E.W. Steinkuller, D.D. Williams, R.R. Miller, J. Chem. Eng. Data, 11, 309-314 (1966)
J. Chem. Eng. Data, 11, 315-320 (1966)
J. Chem. Eng. Data, 11, 320-322 (1966).
- 40b. C.T. Ewing, J.P. Stone, J.R. Stann, R.R. Miller, J. Chem. Eng. Data, 11, 468-473 (1966).
41. I.K. Kikoin, A.P. Senchenkov, Fiz. Metall. Metalloved, 24, 843 (1967), Phys. Metals Metallogr., 24, 74-89 (1967).
42. D.R. Postill, R.G. Ross, N.E. Cusack, Adv. Phys., 16, 493 (1967); Philos. Mag., 18, 519 (1968).
- 43a. J.S. Rowlinson, Liquids and Liquid Mixtures, (Butterworth, London 1959).
- 43b. E. Kordes, Z. Elektrochem., 57, 731-738 (1953).
44. L. Cailletet, E. Mathias, Comptes Rendus, 102, 1202-1207 (1886).
45. R.N. Lyon, Liquid Metals Handbook, U.S. Government Printing Office, Washington (1950), 2nd revised Ed. (1954).
46. W.H. Evans, R. Jacobson, T.R. Munson, D.D. Wagman, J. Res. NBS 55/2, 83-96 (1955).
47. Gmelin, Handbuch der Anorganischen Chemie, System-Nummer Li:20 (1960), Na:21 (1966), K:22 (1938), Rb:24 (1937), Cs:25 (1938), Verlag Chemie, GmbH Weinheim/Bergstraße.
48. R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley, D.D. Wagman, Selected Values of the Thermodynamic Properties of the Elements, American Soc. for Metals, Metals Park, Ohio (1973).
49. N.B. Vargaftik, Tables on the Thermophysical Properties of Liquids and Gases, John Wiley & Sons, Inc. (1975).
50. O.J. Foust, Sodium-NaK Engineering Handbook, Gordon and Breach, Science Publishers, Inc. New York (1979).
51. H.D. Luedemann, G.C. Kennedy, J. Geophys. Res., 73, 2795-2805 (1968).
52. E.E. Shpil'rain, K.A. Yakimovitch, E.E. Toskij, D.L. Timrot, V.A. Fomin, Thermophysical Properties of Alkali Metals, Standard Press, Moscow (1970).

53. G.J. Zukowsky, Z. anorg. allgem. Chem., 71, 403-418 (1911).
54. L. Losana, Gazzetta Chimica Italiana, 65, 851-864, (1935).
55. S.B. Kilner, J. Am. Chem. Soc., 77, 5221 (1952).
56. T.B. Douglas, L.F. Epstein, J.L. Dever, W.H. Howland, J. Am. Chem. Soc., 77, 2144 , (1955).
57. D.V. Keller jr., F.A. Kanda, A.J. King, J. Phys. Chem., 62, 732 (1958).
58. Ye. G. Ponyatovskii, Fiz. metal. metalloved., 11, 476-477 (1961), engl. translation, Phys. Met. and Metallogr., 11, 146-147 (1961).
59. W.D. Weatherford Jr, R.K. Johnston, M.L. Valtierra, J.W. Rhoades, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio, Report ASD-TDR-63-413 (1963).
60. P. Hubberstey, R.J. Pulham, A.E. Thunder, J. Chem. Soc. Far. Trans., 72, 431 (1976).
61. E. Rengade, Compt. Rend., 156, 1897 (1913), Bull. Soc. Chimique, 15, 130-147 (1914).
62. E. Griffiths, Proc. Roy. Soc. London, 89A, 561-574 (1914).
63. P.W. Bridgman, Phys. Rev., 3, 153-203 (1914), 27, 68-86 (1926).
64. W. Edmonson, A. Egerton, Proc. Roy. Soc., A 113, 520-533 (1927).
65. R. Ladenburg, E. Thiele, Z. Phys. Chem., B7, 161-187 (1930).
66. D.C. Ginnings, T.B. Douglas, A.F. Ball, J. Res. NBS, RP 2110 45, 23-33 (1950).
67. D.L. Martin, Phys. Rev., 154, 571-575 (1967).
68. D.R. Anderson, J.B. Ott, J.R. Goates, H.T. Hall jr., Techn. Rep. COO-1707-9, Brigham Young Univ. (1970).
69. P.W. Mirwald, G.C. Kennedy, J. Phys. Chem. Solids, 37, 795-797 (1976).
70. H. Kamioka, J. Phys. Soc. Japan, 52, 2433-2439 (1983).
71. L.G. Carpenter, C.J. Steward, London Phil. Mag. and J. Sci., 27, 551-564 (1939).
72. T.B. Douglas, A.F. Ball, D.C. Ginnings, W.D. Davis, J. Am. Chem. Soc., 74, 2472 (1952).
73. N.S. Grachev, P.L. Kirillov, Inzh. Fiz. Zh., 3, 62 (1960).
74. A.S. Basin, S.P. Volchkova, A.N. Soloviev Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, 10, 128-133 (1969), translated in J. Appl. Mech. and Tech. Phys., 10, 961-966 (1969).
75. J.B. Ott, J.R. Goates, Tech. Prog. Report COO-1707-9 (1970).
J.R. Goates, J.B. Ott, C.C. Hsu, Trans. Far. Soc., 66, 25 (1970).
76. T.M. Dauphinee, D.L. Martin, H. Preston-Thomas, Proc. Roy. Soc., A 233, 214-222 (1955).
77. J.D. Filby, D.L. Martin, Proc. Roy. Soc., A 284, 83-107 (1965).
78. D.L. Martin, Can. J. Phys., 48, 1327-1339 (1970).
79. J.H. De Boer, J. Broos, H. Emmens, Z. anorg. u. allgem. Chem., 191, 113-121 (1930).
80. M.E. Rinck, Comptes Rendus, 199, 1217-1219 (1934).
81. J.B. Taylor, I. Langmuir, Phys. Rev., 51, 753 (1937).
82. K. Clusius, H. Stern, Z. angew. Phys., 6, 194-196 (1954).
83. G.C. Kennedy, A. Jayaraman, R.C. Newton, Phys. Rev., 126, 1363-1366 (1962).
84. C.T. Heycock, F.E. Lamplough, Proc. Chem. Soc. London, 28, 3 (1912).
85. M.M. Makanski, C.H. Muendel, W.A. Selke, J. Phys. Chem., 59, 40-42 (1955).

86. C.F. Bonilla, D.L. Sawhney, M.M. Makansi, ASM Trans. Quaterly, 55, 877-890 (1962).
87. E.S. Sowa, Nucleonics, 21, 76-77 (1963).
88. K.J. Bowles, L. Rosenblum, J. Chem. engineering data, 10, 321-322 (1965). NASA TND-2849, Lewis Research Center, Cleveland, Ohio (1965)
89. P.Y. Achener, J.T. Jouthas, Aerojet-General Nucleonics Report, AGN-8191/I (1966).
90. Yu.K. Vinogradov, L.D. Volyak, Teplofizika Vysokikh Temperatur, 4, 50-54 (1966).
91. A.K. Fischer, Rev. Sci. Instr., 37, 717-719 (1966).
92. P.Y. Achener, A.R. Miller, D.L. Fisher, Aerojet-General-Corp., Report AGN 8194/II (1967),
93. S. Das Gupta, Thesis, Columbia University, New York (1977).
94. F. Petiot, J.M. Seiler, High Temp. - High Press., 16, 289-293 (1984).
95. L.I. Cherneeva, V.N. Proskurin, Teplofizika Vysokikh Temperatur 10, 674 (1972); High Temperature 10,
96. L.I. Cherneeva, V.N. Proskurin, Teplofizika Vysokikh Temperatur, 10, 765-770 (1972), engl. transl. High Temperature, 10, 687-691 (1972).
97. A.M. Belova, E.E. Shpil'rain, V.I. Shkermontov, A.G. Mozgovoi, Tep. Vys. Temp., 18/2, 290 (1980).
98. P.Y. Achener, Aerojet-General-Corp., Report AGN-8090/I (1964).
99. L.D. Volyak, Yu. K. Vinogradov, V.M. Anisimov, Teplofizika Vysokikh Temperatur, 6, 754-755 (1968), engl. transl. High Temperature, 6, 719-720 (1968).
100. O. Ruff, O. Johannsen, Ber. D. Chem. Ges., 38, 3601 (1905).
101. F. Tepper, A. Murchinson, J. Zelenak, R. Roehlich, V. May, Report AFML-TR-65-99 (1965).
102. P.Y. Achener, W.V. Mackewicz, D.L. Fischer, D.C. Camp, Aerojet-General-Corp., Report AGN-8195/I (1968).
103. C.T. Ewing, J.P. Stone, J.R. Spann, R.R. Miller, J. Chem. Eng. Data, 11, 473-480 (1966).
104. E.E. Shpil'rain, A.M. Belova, Tep. Vys. Temp., 5, No. 3, 531-532 (1967), engl. transl. High Temperature, 5, 477-478 (1967).
105. E.E. Shpil'rain, E.V. Nikanorov, Teplofizika Vysokikh Temperatur, 10, 297-304 (1972), engl. transl. High Temperature 10, 261-267 (1972), Proc. 5th Symp. Thermophys. Prop. Boston 1970, 450-460 (1970).
106. J.F. Walling, J. Phys. Chem., 67, 1380-1382 (1963).
107. E.E. Shpil'rain, E.E. Totskii, V.A. Shereshevskii, Tep. Vys. Temp., 6, No. 5, 924-926 (1968), High Temperature, 6, 885-887 (1968).
108. C.T. Ewing, J.R. Spann, J.P. Stone, R.R. Miller, J. Chem. Eng. Data, 16, 27-30 (1971).