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THERMAL PROPERTIES OF SUPERHEATED POTASSIUM VAPOR AT TEMPERATURES TO 2150 K AND PRESSURES TO 10 MPa.

1. AN EXPERIMENTAL INVESTIGATION OF THE THERMAL PROPERTIES

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Data have been obtained for the PvT relationship of superheated potassium vapor over ranges of the parameters of state not previously investigated; a modified constant-volume piezometric method has been used with an error not exceeding 1%.

The scanty experimental work on the investigation of the thermal properties of potassium in the gaseous phase [1-5] was carried out mainly in the U.S.A. in the middle 1960s (see Table 1). A critical evaluation of each of these studies is given in [6], and conclusions are drawn as to the accuracy of the experimental data based on a graphical analysis and comparison of the interconsistency. As a result of this analysis paper [2] was taken to be the most accurate investigation while the data of [1] and [5] had the largest errors. For making thermodynamic generalizations experimental data are necessary which have high dependability and sufficient measurement accuracy. Such investigations include papers [2] and [3], the experimental data of which provide a mass of experimental points which are suitable for thermodynamic generalization.

However, as can be seen from Table 1 these data were obtained over limited ranges of the state parameters. The authors of references [2-4] who used in their investigations the method of constant-volume piezometry with a zero-membrane in the hot zone were not able to carry out measurements at high values of the parameters. Tests show that a membrane placed in the hot zone operates unreliably, deforms, and shifts its zero position. In order to describe the thermodynamic properties of potassium vapor over a wide range of the parameters of state additional experimental investigations are required at high temperatures and pressures. In this connection, a method of constant-volume piezometry with the zero-membrane in the cold zone has been developed in the MAI [Sergo Ordzhonikidze Aviation Institute, Moscow] for the measurement of the specific volumes of metal vapors [7].

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TABLE 1. Experiments to Investigate the Thermal Properties of Superheated Potassium Vapor

Lit. source	Range investigated		Error with respect to compres. Z, % [6]	Method
	with respect to temp. T,K	with respect to pres.P, MPa		
[1]	1134—1422	0,12—1,12	—	modified constant-volume piezometer
[2]	1150—1700	0,24—2,78	0,5—0,7	constant-volume piezometer with zero-membrane in hot zone
[3]	937—1407	0,03—0,77	1,5—7,0	ditto
[4]	1150—1481	0,24—1,43	0,5—2,0	»
[5]	1423—2075	1,25—7,24	—	modified constant-volume piezometer

In an experimental apparatus operating according to this method an investigation has been carried out of the thermal properties of cesium vapor up to temperatures and pressures close to the critical zone with an error not exceeding 1% over the entire measurement range. It should be noted that the use of this method for investigating rubidium, potassium, sodium, and lithium gives rise to certain difficulties as the atomic mass of the alkali metal decreases. Since the atomic mass decreases in the alkali metal group from cesium to lithium it is necessary to increase the volume of the working chamber of the piezometer in proportion to this decrease in order to maintain the measurement accuracy (relative to cesium). For example, for rubidium the volume of the piezometer chamber should be $^{132}Cs/^{85}Rb \approx 1.5$ times larger than in the experiments with cesium, and for potassium it should be 3.5 times larger. A consequence of the increase of the volume of the working chamber of the piezometer is an increase in the size of the heater and its power, so that the heat transfer increases and the temperature field over the length of the working chamber of the piezometer changes for the worse. In addition, and this is particularly troublesome, there is an increase in the volume of the relief chamber (in which the piezometer, heater, heat screen, etc. are placed), in which the pressure of argon must reach 15 MPa at temperatures above 2000 K [8]. It becomes obvious that the use of this method for investigating the thermal properties of lithium would cause considerable technical difficulties in the experimental equipment.

In setting up the experimental equipment for investigating potassium, in addition to making the constructional changes connected with the increase of the volume of the working chamber which are listed above, the method of charging the liquid potassium into the piezometer was also improved. For this purpose a dosimetric device was constructed by means of which liquid potassium could be fed into the piezometer at any required dosage [8, 9].

Earlier, as indicated in [7], the charging of a specified mass of cesium into the piezometer was carried out in a special unit, and then the assembly of the experimental equipment was carried out, which consumed a considerable amount of time. For carrying out the complete investigation it was necessary to have 10-15 single-use piezometers. Thus, the use of the dosimetric device considerably reduced the difficulty and cost of preparing the equipment for the experiments and also eliminated the errors which unavoidably arise during the utilization of single-use piezometers. A flowsheet of the equipment, descriptions of the operation of the individual sections, and the procedure for carrying out the experiments are given in [8-10].

An estimate of the relative error $\Delta Z/Z$ of the measurements of the compressibility coefficient $Z = \mu Pv/RT$ was calculated from the relative errors in the pressure $\Delta P/P$, temperature $\Delta T/T$, and specific volume $\Delta v/v$, i.e., in the parameters which can be measured directly [7].

In order to improve the accuracy of the pressure measurements a type IPD pressure transducer with a Shch 1413 voltmeter was used instead of an MO type manometer; the 0.1% measurement accuracy of this arrangement was higher than that of a standard manometer.

The nonuniformity of the temperature field over the length of the working chamber of the piezometer introduces a considerable error in the calculation of $\Delta Z/Z$. By introducing an additional guard heater the temperature gradient over the length of the heater and chamber was reduced to 25°C at pressures of 9-10 MPa and temperatures of 2100-2200 K. As regards the relative error of the specific volume $\Delta v/v$, this arises as a result of errors in the volume of the working chamber of the piezometer $\Delta V/V$ and in the mass of potassium vapor in it $\Delta m_V/m_V$. In connection with this, the volume of the working chamber was increased by ≈3.5 times, as mentioned above, and amounted to $1.07 \cdot 10^{-4}$ m^3.

TABLE 2. Experimental Data from PvY Measurements on Superheated Potassium Vapor

No.	P, MPa	T, K	$v \cdot 10^3$, $m^3 \cdot kg^{-1}$
$m \cdot 10^3 = 1{,}225$ kg			
1	1,4664	1476	178,5
2	1,6380	1524	165,9
3	1,7646	1570	159,9
4	1,8726	1605	155,1
5	2,0004	1648	149,5
6	2,1327	1696	143,6
7	2,3106	1772	141,0
8	1,4642	1835	137,6
9	2,6298	1898	134,2
10	2,7370	1946	132,7
11	2,9052	1996	129,3
12	3,0342	2046	127,4
13	3,1002	2072	126,4
$m \cdot 10^3 = 1{,}737$ kg			
14	2,5743	1577	103,3
15	2,6261	1593	102,6
16	2,7020	1615	101,4
17	2,8107	1644	99,83
18	2,8676	1660	99,16
19	2,9466	1683	98,16
20	3,0022	1700	96,95
21	3,0552	1713	96,54
22	3,0686	1718	96,05
23	3,0830	1724	95,99
24	3,2120	1760	94,73
25	3,3956	1815	92,90
26	3,5846	1876	91,11
27	3,8858	1954	88,40
28	4,2656	2058	85,04
29	4,4442	2103	83,57
30	4,3980	2092	83,97
31	4,2596	2056	$85{,}0_4$
32	4,0634	2002	$86{,}8_3$
$m \cdot 10^3 = 2{,}145$ kg			
33	3,6521	1675	74,83
34	3,7243	1689	73,96
35	3,7847	1704	73,46
36	3,8825	1722	72,82
37	3,9562	1740	72,33
38	4,0258	1754	71,90
39	4,0816	1770	71,48
40	4,1524	1785	71,11
41	4,2094	1795	70,79
42	4,3576	1828	69,79
43	4,5028	1863	69,08
44	4,5562	1881	68,80
45	4,7668	1930	67,78
46	5,0410	1990	66,70
47	5,1634	2014	66,13
48	5,1430	2010	66,19
49	5,2888	2046	65,57
50	5,3056	2050	65,42
$m \cdot 10^3 = 2{,}607$ kg			
51	4,9124	1768	57,06
52	5,0103	1788	56,76
53	5,0930	1805	56,47
54	5,1979	1826	56,13
55	5,3006	1845	55,79
56	5,3874	1862	55,51
57	5,4752	1878	55,26
58	5,5515	1895	55,07
59	5,6275	1911	54,85
60	5,6900	1925	64,66
61	5,7868	1943	54,45
62	5,8583	1955	54,34
63	5,9981	1984	53,98
64	6,0899	2005	53,75
65	6,1830	2026	53,48
66	6,298	2047	53,26
67	6,533	2094	52,61
68	6,654	2118	52,36
$m \cdot 10^3 = 3{,}073$ kg			
69	7,693	2132	44,19
$m \cdot 10^3 = 3{,}538$ kg			
70	7,254	1917	39,33
71	7,468	1947	38,91
72	7,576	1963	38,77
73	7,680	1978	38,60
74	7,812	1994	38,41
75	7,893	2007	38,31
76	7,994	2023	38,16
77	8,124	2038	37,98
78	8,231	2054	37,83
79	8,335	2070	37,72
80	8,429	2086	37,56
81	8,507	2095	37,44
82	8,635	2113	37,38
83	8,772	2134	37,26
$m \cdot 10^3 = 3{,}996$ kg			
84	8,495	1983	33,72
85	8,658	2003	33,55
86	8.774	2019	33,45
87	8.927	2038	33,30
88	9,046	2052	33,20
89	9,163	2066	33,08
90	9,275	2080	32,98
91	9,370	2093	32,89
92	9,487	2108	32,79
93	9,644	2126	32,66
94	9,841	2151	32,45
95	9.962	2162	32,43
96	10,04	2167	32,40
$m \cdot 10^3 = 1{,}437$ kg			
97	2,2067	1612	129,4
98	2,2643	1636	127,9
99	2,2937	1647	127,3
100	2,3477	1662	125,7
101	2,4623	1703	123,5
102	2,5763	1739	120,7
103	2,7196	1791	117,9
104	2,8298	1828	115,8
105	2,9223	1857	114,2
106	3,0530	1897	111,9
107	3,2369	1955	109,2
108	3,3689	1997	107,2
109	3,5045	2043	105,6

TABLE 2 (continued)

No.	P, MPa	T, K	$v \cdot 10^3$, $m^3 \cdot kg^{-1}$
$m \cdot 10^3 = 1{,}585$ **kg**			
110	2,1902	1538	120,4
111	2,2734	1558	118,5
112	2,3541	1583	116,6
113	2,4348	1607	115,0
114	2,4807	1630	113,9
115	2,5501	1645	112,3
116	2,5999	1660	111,6
117	2,6722	1686	110,5
118	2,6941	1697	110,2
119	2,7115	1702	109,9
120	2,7589	1716	109,1
121	2,7985	1726	108,4
122	2,9233	1766	106,4
123	3,1452	1833	103,0
124	3,3762	1906	99,88
125	3,7555	2017	95,83
126	4,0549	2104	92,98
127	3,2213	1865	102,1
128	2,8134	1730	108,1
$m \cdot 10^3 = 1{,}924$ **kg**			
129	3,0729	1626	87,62
130	3,1447	1643	86,83
131	3,1923	1658	86,33
132	3,2836	1680	85,38
133	3,3768	1702	84,51
134	3,4335	1716	83,91
135	3,4963	1730	83,38
136	3,5540	1745	82,74
137	3,5888	1753	82,58
138	3,6260	1764	82,27
139	3,6718	1780	82,16
140	3,7088	1793	82,02
141	3,7796	1809	81,37
142	4,0076	1870	79,66
143	4,4342	1965	76,30
144	4,8110	2066	74,45
145	4,9850	2111	73,60
146	4,4774	1977	76,01
147	4,0718	1883	79,14
$m \cdot 10^3 = 2{,}384$ **kg**			
148	4,3240	1727	64,19
149	4,3938	1742	63,79
150	4,4665	1758	63,48
151	4,5352	1773	63,19
152	4,6134	1789	62,86
153	4,7381	1813	62,40
154	4,7901	1828	62,11
155	4,8657	1842	61,83
156	4,9320	1855	61,59
157	4,9725	1865	61,42
158	5,0054	1871	61,36
159	5,0978	1892	61,04
160	5,1624	1905	60,74
161	5,2074	1916	60,61
162	5,3372	1946	60,11
163	5,3832	1953	59,98
164	5,5188	1985	59,53
165	5,7868	2034	58,66
166	5,9430	2066	58,07
$m \cdot 10^3 = 2{,}842$ **kg**			
167	5,5691	1808	51,24
168	5,6636	1824	50,96
169	5,7528	1843	50,71
170	5,8494	1861	50,43
171	5,9402	1879	50,18
172	6,036	1898	49,96
173	6,144	1919	49,70
174	6,283	1946	49,37
175	6,354	1963	49,12
176	6,450	1979	48,92
177	6,601	2008	48,62
178	6,790	2037	48,08
179	6,918	2059	47,79
180	7,068	2081	47,58
181	6,849	2051	47,99
182	6,428	1977	49,00
$m \cdot 10^3 = 3{,}316$ **kg**			
183	6,833	1887	42,30
184	6,908	1903	42.14
185	7,025	1919	41,93
186	7,107	1935	41,76
187	7,226	1953	41,55
188	7,310	1968	41,40
189	7,414	1986	41,23
190	7,484	1998	41,08
191	7,581	2015	40,94
192	7,653	2026	40,84
193	7,700	2037	40,75
194	7,877	2062	40,56
195	7,953	2074	40,45
196	8,070	2089	40,18
197	8,155	2104	40,11
198	8,241	2118	40,05
199	8,235	2113	40,07
200	8,061	2088	40,15
201	7,877	2062	40,49

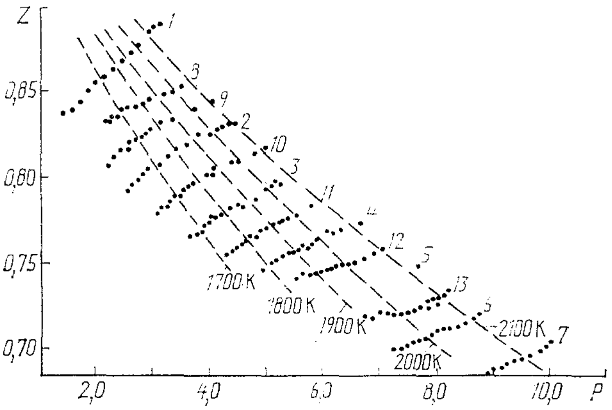

Fig. 1. Dependence of the compressibility coefficient z on the pressure P, MPa, for superheated potassium vapor.

TABLE 3. Evaluation of the Measurement Error of the PvT Data for Superheated Potassium Vapor, %

Number of experiment	$\Delta T/T$	$\Delta P/P$	$\Delta v/v$	$\Delta Z/Z$
1	0,43...0,48	0,14...0,09	0,91...0,56	1,12...0,81
2	0,44...0,49	0,10...0,08	0,55...0,42	0,78...0,67
3	0,45...0,48	0,08	0,43...0,34	0,69...0,65
4	0,47...0,49	0,08...0,23	0,34...0,29	0,65...0,67
5	0,50	0,19	0,29	0,67
6	0,50...0,49	0,18...0,17	0,28	0,66...0,65
7	0,50...0,49	0,15	0,26	0,64...0,63
8	0,44...0,48	0,11...0,09	0,68...0,49	0,90...0,76
9	0,45...0,49	0,10...0,08	0,62...0,44	0,85...0,73
10	0,44...0,49	0,09...0,08	0,47...0,36	0,72...0,67
11	0,46...0,48	0,08	0,37...0,32	0,66...0,64
12	0,46...0,48	0,24...0,21	0,33...0,29	0,68...0,66
13	0,49	0,19...0,18	0,29...0,27	0,66...0,65

The results of the PvT measurements on superheated potassium vapor are shown in Table 2. Over the temperature and pressure ranges 1480-2170 K and 1.5-10 MPa 201 experimental points were recorded on 13 isochores. Measurements were carried out both with the temperature increasing and with the temperature decreasing, and the experimental points fell with good accuracy along a single line. The potassium investigated in the experiments corresponded to Technical Specification [TU] 48-3-53-75 and contained 0.08% sodium.

The evaluation of the experimental error was carried out for a confidence coefficient of 0.95 using the relationships derived in [7] (see Table 3). In this table experiment No. 1 corresponds to the experimental points of Table 2 having a mass of potassium in the piezometer $m = 1.225 \cdot 10^{-3}$ kg, experiment No. 2 to $m = 1.737 \cdot 10^{-3}$ kg, experiment No. 3 to $m = 2.145 \cdot 10^{-3}$ kg, etc. It follows from Table 3 that the largest errors ($\Delta Z/Z = 1.1$-0.8%) are found in the data for experiments Nos. 1, 8, and 9, which is related to the small ratio of the mass of potassium in the liquid and vapor phases. As the mass of potassium in the piezometer increases, the ratio increases, and the relative error in the specific volume $\Delta v/v$ decreases. When $P > 5$ MPa the term $\Delta T/T$ has the largest error, which is related to the nonuniformity of the temperature field over the length of the piezometer chamber and to the accuracy of measuring the temperatures.

A qualitative representation of the experimental results is given by the dependence of the compressibility coefficient Z on the pressure P which is constructed from the experimental data (see Fig. 1).

A comparison of the experimental data obtained for the PvT relationship of potassium up to $T = 1700$ K and $P = 2.8$ MPa with the PvT data of reference [2] shows that they agree with each other to within the accuracy limits of the experiments which have been carried out. The data of [5] for $P > 6$ MPa agree within 3-6%. At smaller pressures the deviation does not exceed 1%.

Thus, as a result of the investigation new experimental data of sufficient reliability have been obtained on the thermal properties of superheated potassium vapor which can be used for setting up equations of state and tables of thermodynamic functions for the vapor of potassium; the results can also be used in the development of analogous experimental equipment for measuring the specific volumes of various metals.

NOTATION

P pressure; T temperature; v specific volume; Z compressibility coefficient; μ molecular weight; R universal gas constant; m mass of potassium in piezometer; m_v mass of potassium vapor in piezometer; V volume of the working chamber of the piezometer.

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THERMODYNAMIC PARAMETERS OF HYDROCARBONS IN THE CRITICAL RANGE.

1. n-OCTANE AND n-NONANE

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UDC 536.71

Scale equations of state have been derived for normal octane and nonane, which describe the thermal and caloric properties of those substances with an error close to the error of experiment.

Measurements have been made [1-3] on the P, ρ, T, and C_p dependence for normal octane and nonane in wide ranges around the critical points. In [1, 2], the P, ρ, and T data were recorded with a constant-volume piezometer relieved from pressure. The errors were 0.05-0.10% for pressure, 0.02-0.03 K, and 0.1% for the density (without allowance for the reference error). In [3], a flow adiabatic calorimeter was used to measure C_p. I estimate the errors to be 0.08-0.15% in pressure, 0.02-0.03 K, and 1.0-4.0% for the specific heat. The purity in both cases was better than 99.8%. In [4], the isochoric specific heat C_v was determined for those substances in the critical range, but those data are unreliable because the purity was not examined and no check was made on the onset of thermal decomposition. The [1-3] data have enabled me to construct equations of state in the critical region for n-octane and n-nonane. I used a scale equation of state [5], which in parametric form is

$$\Delta\mu = ar^{\beta\delta}\theta(1-\theta^2) + cr^{\beta\delta+\Delta}\theta + r^{2\nu+2\beta-1}[d(1+e_1b^4\theta^4) + fb^2\theta^2(1+e_2b^2\theta^2)], \tag{1}$$

$$\tau = r(1-b^2\theta^2), \tag{2}$$

$$\Delta\rho = kr^{\beta}\theta - B_3\tau. \tag{3}$$

Here $\Delta\mu = [\mu(\rho, T) - M_0(\tau)]\rho_c/P_c$, $\tau = T/T_c - 1$, and $\Delta\rho = \rho/\rho_c - 1$ are correspondingly the dimensionless chemical potential, the temperature, and the density; r and θ are polar coordinates characterizing the point on the thermodynamic surface, and in particular, r defines the distance of that point from the critical one and θ the angle of rotation.

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