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Experimental Research on Specific Volumes of Rubidium and Potassium Vapors

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Results are reported of an experimental study of superheated rubidium vapor in the temperature range 1450–2000 K and pressure range 1.7–5.2 MPa and potassium in the range 1500–2100 K and 1.4–4.0 MPa. The experiments have been performed with an apparatus adaoted to implement a modified constant-volume piezometer technique, where the sensing element of a pressure transducer represented by a diaphragm is placed in a low-temperature zone. A dosing device is described which permits the performance of accurate measurements of the mass of the metal in the piezometer chamber. The present results are in good agreement with those reported by other investigators in the overlaping temperature and pressure ranges.

KEY WORDS: dosing device; piezometer; potassium; *PVT* measurements; rubidium; specific volume; superheated vapor.

1. INTRODUCTION

So far, data on experimental research of the *PVT* relationship for superheated rubidium vapor have been limited in terms of both the number of papers published [1, 2] and the range of investigated temperatures, $T = 920$–1450 K, pressures, $P = 0.053$–1.5 MPa, and specific volumes, $v = 0.084$–$0.465\ \mathrm{m^3 \cdot kg^{-1}}$. Measurement error analysis is not given in these papers.

The most reliable results of similar investigations of potassium vapor are those presented in Ref. 3 spanning the following range of the state parameters: $T = 1150$–1700 K, $P = 0.2$–2.8 MPa, and $v = 0.10$–$0.94\ \mathrm{m^3 \cdot kg^{-1}}$. The authors have estimated the accuracy of the experimental data from the compressibility factor as 0.26–0.35%.

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An analysis of the equations of state developed for rubidium and potassium vapors appears in Ref. 4. Moreover, a semiempirical equation of state has been obtained, and thermodynamic properties have been tabulated in Ref. 5 for potassium up to $P = 5.0$ MPa and $T = 2000$ K.

The purpose of the present work is to make an experimental investigation of specific volumes for rubidium and potassium vapors over a greater range of temperature and pressures.

2. EXPERIMENTAL TECHNIQUE

In order to perform the experiments, the authors have employed an apparatus adapted to implement a modified constant-volume piezometer technique, wherein a diaphragm representing a sensing element of a pressure transducer is placed in a low-temperature zone. Such a location for a heavy-duty structural member has enabled substantial prolongation of the service life, improving the reliability of the apparatus. The flow diagram and description of the apparatus, as well as the experimental techniques, are given in the literature [6, 7]. Since the time of publication of these papers, the design of the apparatus has been further improved. The most recent design is shown in Fig. 1.

Distinct from the design described in Refs. 6 and 7, we have improved the accuracy of pressure measurements by using a digital measurement system having an accuracy of 0.06%. The volume of the piezometer used was 42.741 cm^3 for rubidium and 107.071 cm^3 for potassium.

As described in Refs. 6 and 7, to load the piezometer with metal use was made of a spcial-purpose stand. The amount of substance to be analyzed was derived from the difference between the weight of the empty and that of the filled piezometer. The design of the apparatus was such that in order to make experiments with diverse masses, one had to dismantle the apparatus partially, depressurizing the piezometer, and repeat the loading and weighing runs. It is clear that the above steps take a rather long time, complication the entire experiment. A special-purpose measuring or dosing device has been designed to eliminate the above disadvantages (see Fig. 1). The dosing device contains bellows (14) welded to each other to form a pressure-tight assembly placed inside a detachable housing (17). When the shutoff cock (12) is open the cavities of the bellows and the chamber of the piezometer (1) are brought in communication with each other through a stainless-steel capillary tube. The opposite end of the assembly is made to carry a fine adjustment screw (15) with a nut (16) made in the form of a shaft, with 0.15-mm thread pitch. The shaft is connected via a hinge (18) to a revolution counter, not shown. Thus, rotation of the shaft (16) is converted into the translational motion of the screw

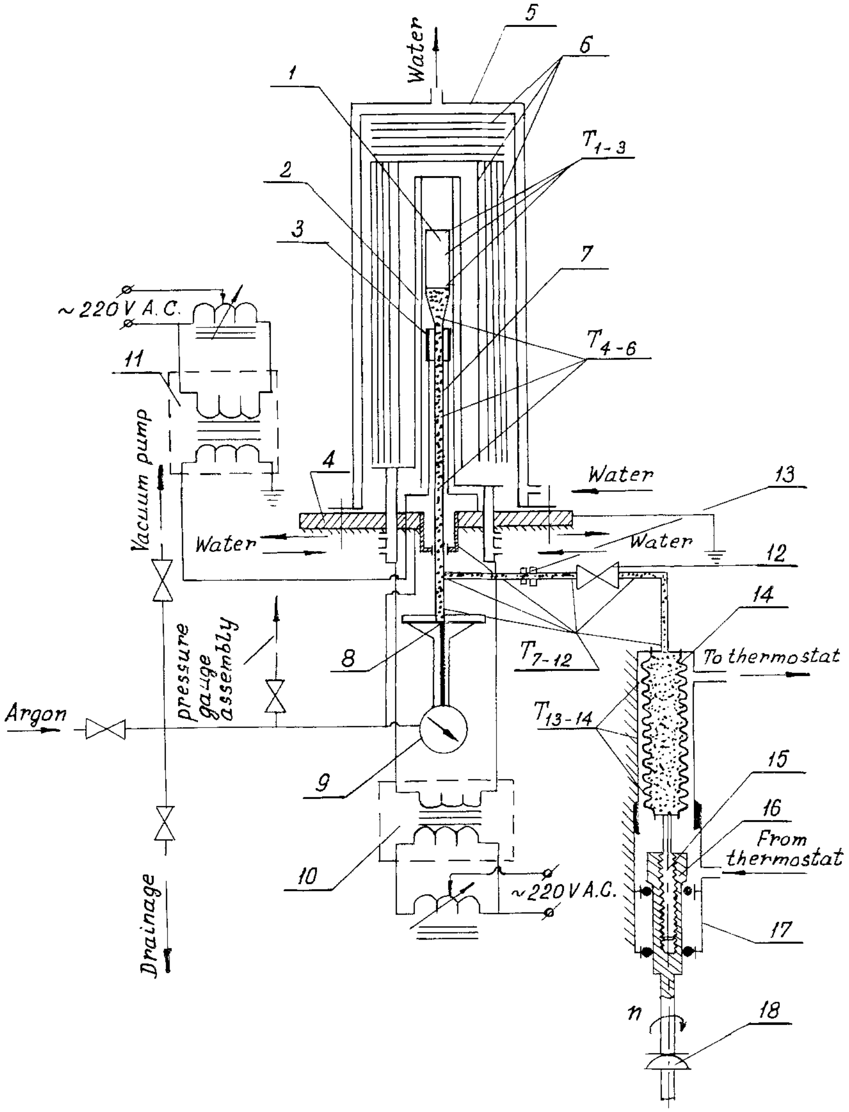

Fig. 1. Flow diagram of the experimental apparatus. 1, Piezometer chamber; 2, heater; 3, extra heater; 4, plate; 5, housing; 6, thermal screens; 7, capillary tubes; 8, diaphragm; 9, indicator body; 10, step-down transformer for the heater; 11, step-down transformer for an extra heater; 12, shutoff cock; 13, detachable joint; 14, bellows; 15, fine adjustment screw; 16, nut; 17, detachable housing of the dosing device; 18, hinge; T_{1-3} and T_{4-6}, tungsten–rhenium thermocouples; T_{7-12} and T_{13-14}, chromel–alumel thermocouples.

(15), resulting in the volume of the bellows assembly being changed, thus changing the amount of metal loated into the bellows cavity accordingly.

The dosing device has been thoroughly graduated beforehand. As a result, we have plotted $\Delta V'$ as a function of n, $\Delta V' = f(n)$, where n is the number of revolutions counted and $\Delta V'$ is the variation in the inner volume of the bellows assembly. Calibration was made with distilled water. The results of the calibration were processed on a computer using the last-squares technique, yielding an approximation function which defines the entire multitude of points within an accuracy of better than 0.2%.

Metal is loaded into the dosing device at a special-purpose stand. Once the substance to be analyzed is loaded, the dosing device is connected to the piezometer. The piezometer cavity is evaluated down to 10^{-5} mm Hg. A thermostat is used to heat up the dosing device to a temperature which is 40–50 K higher than the melting point of the metal under investigation, and the capillary tube and piezometer are also held at this teperature. With the shutoff cock open, the fine adjustment screw is rotated to supply a batch of the analyzed metal into the piezometer, the mass of the metal having been found from the calibration curve.

In order to equalize the temperature over the height of the instrument in the experiments with potassium, the apparatus is made to comprise an extra heater (3) (see Fig. 1). The heater is connected to a separate power source.

In other respects, the experimental procedure is identical to that used in Refs. 6 and 7.

3. EXPERIMENTAL RESUTS

Rubidium used in the experiments included the following impurities: K, 0.003%; Na, 0.03%; and Cs, 0.03%. Potassium contained 0.008% Na. For rubidium the results of investigations are given in Table I, spanning the range up to $T = 2100$ K and $P = 5.2$ MPa. For potassium the experiments have also been made using three batches up to $T = 2110$ K and $P = 5.0$ MPa. The results of the measurements are given in Table II.

4. DISCUSSION

It is a common practice to estimate inaccuracies in experimental data related to the PVT relationships from the compressibility factor $Z = Pv/RT$, where $R = 8314/\mu$, a gas constant, and μ is the molecular weight of the metal being investigated. The above gives

$$\Delta Z/Z = Q\sqrt{(\Delta P/P)^2 + (\Delta T/T)^2 + (\Delta v/v)^2} \qquad (1)$$

For the confidence level of 0.95, coefficient $Q = 1.1$. $\Delta P/P$ (0.06%), $\Delta T/T$ (0.41–0.46%), and $\Delta v/v = \sqrt{(\Delta V/V)^2 + (\Delta m/m)^2}$ are the errors in measured pressures, measured temperatures, and determined specific volume, respectively. $\Delta V/V$ (0.04–0.05%) is the uncertainty in the estimation of the volume of the piezometer due to errors in weighing and

Table I. Specific Volume of Rubidium

Item	P (MPa)	T (K)	v ($m^3 \cdot kg^{-1}$)
	Test mass $m = 1.201$ g		
1	0.7372	1286	0.1521
2	0.8842	1354	0.1317
3	1.0171	1416	0.1187
4	1.4872	1622	0.09172
5	2.0338	1828	0.07610
6	2.7616	2164	0.06500
7	2.6086	2088	0.06670
	Test mass $m = 1.609$ g		
1	1.8130	1474	0.06489
2	1.9747	1518	0.06162
3	2.0920	1555	0.05980
4	2.3533	1648	0.05622
5	2.5336	1698	0.05392
6	2.8603	1800	0.05086
7	3.1720	1876	0.04843
8	3.7486	2059	0.04536
9	4.0012	2158	0.04394
10	3.8932	2123	0.04457
11	3.5788	1986	0.04549
	Test mass $m = 2.017$ g		
1	3.2707	1607	0.04006
2	3.4165	1634	0.03944
3	3.5827	1665	0.03861
4	3.8137	1708	0.03763
5	3.9193	1737	0.03727
6	4.0525	1774	0.03671
7	4.1719	1819	0.03628
8	4.3147	1838	0.03578
9	4.4653	1868	0.03540
10	4.6261	1907	0.03485
11	4.7581	1945	0.03458
12	4.9753	1986	0.03401
13	5.1775	2028	0.03364

Table II. Specific Volume of Potassium

Item	P (MPa)	T (K)	v ($m^3 \cdot kg^{-1}$)
	Test mass $m = 1.225$ g		
1	1.4664	1476	0.1785
2	1.6380	1524	0.1659
3	1.7646	1570	0.1599
4	1.8726	1605	0.1562
5	2.3106	1772	0.1422
6	2.4642	1835	0.1387
7	2.6298	1898	0.1353
8	2.7370	1946	0.1327
9	2.9052	1996	0.1307
10	3.0342	2046	0.1288
11	3.1002	2072	0.1273
	Test mass $m = 1.585$ g		
1	2.5501	1645	0.1123
2	2.5599	1660	0.1160
3	2.6869	1685	0.1099
4	2.6941	1697	0.1095
5	2.7115	1702	0.1092
6	2.7589	1716	0.1082
7	2.7985	1726	0.1075
8	2.9233	1766	0.1056
9	3.1687	1827	0.1019
10	3.4099	1898	0.09730
11	3.7555	2017	0.09469
12	4.0549	2104	0.09249
13	3.2647	1855	0.1002
14	2.7913	1730	0.1081
	Test mass $m = 1.924$ g		
1	3.5540	1745	0.08271
2	3.5888	1753	0.08250
3	3.6260	1764	0.08217
4	3.6806	1780	0.08191
5	3.7088	1793	0.08156
6	3.7796	1809	0.08076
7	4.0076	1870	0.07947
8	4.4342	1965	0.07630
9	4.8110	2066	0.07417
10	4.9850	2111	0.07320
11	4.4774	1977	0.07601
12	4.0610	1883	0.07914

corrections for thermal expansion. $\Delta m/m$ (0.5–1.36% for rubidium and 0.3–0.6% for potassium) is the error in determining the mass of vapor of the metal being investigated. Thus, the total error, as defined from the compressibility factor, is estimated for the experiments with Rb to be 0.7–1.5% and for K to be 0.5 – 0.8%, wherein the greater error is related to measurements with the smallest mass loaded into the piezometer.

Experimental values of v have been compared with those derived from the known equations of state.

The following equation of state has been suggested in Ref. 4 for rubidium:

$$Z=\frac{1+\alpha}{2}+\frac{\Delta B}{2RT}P+\frac{C}{2RT}P^2+\frac{D}{2RT}P^3 \tag{2}$$

where α is the degree of dissociation, and ΔB, C, and D are the semiempirical corrections for pairwise nonbonded couplings, as well as for triple and quadruple couplings. The values of these are given in Ref. 4. Comparison of the experimental values of v for Rb with those obtained from the above equation demonstrates a good agreement (within the limits of 1–1.5%) as applied to points with the test mss $m = 1.201$ g and $m = 1.609$ g. For the test mass $m = 2.017$ g, divergence between the experimental and the calculated values of v increase with P and T from 5 to 10%. This divergence does extend beyond the accuracy limits of the equation, since it has been derived from the joint processing of the PVT data [2] up to 1.5 MPa and pressure of saturated vapor at $T < 1673$ K (up to about 5 MPa).

Experimental results for potassium have been compared with those given in Ref. 5, wherein a semiempirical equation of state for potassium vapors has been obtained from the experimental data on density [3] and potentials of interatomic interactions. This equation is presented in the form of an expansion of pressure and density in terms of the degree of activity of the original atoms (group expansions). Calculated values of v are in agreement with experimental values to within 1–1.5%.

The results of the experimental investigation of rubidium and potassium vapors can be employed in computing thermodynamic properties of these substances.

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