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THERMODYNAMIC PROPERTIES OF CESIUM AND POTASSIUM AT HIGH PRESSURES AND TEMPERATURES

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Results are presented of PVT experiments of cesium and potassium in the gas phase. An equation of state is derived and tables of the thermodynamic properties of cesium vapor are computed. A survey is given of the PVT properties of cesium in the liquid phase.

Several experiments have been conducted to date to determine the thermophysical properties of cesium vapor. Their results may be generalized by the equation of state needed to calculate the thermodynamic properties of cesium vapor. A survey of PVT experiments on cesium is given in the monograph [1]. The most accurate of these experiments was conducted by the method of a constant-volume piezometer, in which an elastic membrane located in the hot zone serves as the pressure transducer. The membrane is unreliable at high temperatures: it changes position, corrodes, and is destroyed. Thus, the physics department at the Moscow Aviation Institute has developed a unit [2] in which the membrane is placed in the cold zone ($t \simeq 50°C$) and the pressure of the cesium vapor is transmitted to the membrane through a column of liquid cesium in a capillary tube. Here, the limiting temperature reached in the experiment is determined only by the thermal stability of the material of the piezometer. Table 1 gives empirical values of PVT parameters obtained on this unit in four series of experiments. The computing error in these experiments for the compressibility factor $z = PV/RT$ is $\Delta z/z = 0.65\%$ with a confidence interval of 0.95.

Several improvements have been made to the design of the unit, the principal one being substitution of a molybdenum heater for the graphite heater. This eliminated the problem of the harmful effect of graphite vapors on the piezometer welds. The unit was used to

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TABLE 1. Empirical PVT Values for Cesium

T, °K	P, bar	V, m³/kg	T, °K	P, bar	V, m³/kg	T, °K	P, bar	V, m³/kg
1366	14,80	0,0494	1619	25,80	0,0326	1763	30,30	0,0303
1443	15,85	0,0490	1629	26,10	0,0323	1780	42,95	0,0191
1466	20,50	0,0367	1637	26,30	0,0322	1793	31,40	0,0300
1480	21,10	0,0364	1645	26,50	0,0320	1802	44,70	0,0189
1503	16,60	0,0486	1653	26,80	0,0319	1809	32,00	0,0299
1510	22,05	0,0352	1695	28,00	0,0312	1835	32,70	0,0298
1528	23,05	0,0346	1697	46,50	0,0161	1873	34,00	0,0296
1532	23,15	0,0344	1705	28,40	0,0311	1930	50,40	0,0185
1549	23,75	0,0341	1723	29,00	0,0308	1940	52,00	0,0184
1557	17,20	0,0480	1735	29,40	0,0307			

obtain empirical PVT data for potassium in the gas phase up to 72 bar (Table 2), as well as P_S—T_S data up to 52 bar (Table 3). These experiments considerably expanded the range of the PVT studies of potassium vapor [3] in the temperature range 1144-1656°K.

The first generalization of several experiments on the thermophysical properties of cesium vapor was made in [4]. Here, on the basis of PVT data and data on the speed of sound in cesium vapor, a special program was used to obtain an equation of state for cesium vapor embracing the region 0.16-33.2 atm and 780-1680°K. The same program was used at the physics department of the Moscow Aviation Institute (MAI), although in this case investigators generalized the more voluminous empirical material from [5-7], the experimental data shown in Table 1 and obtained at the MAI, and the results of experiments on the speed of sound in cesium vapors [8, 9]. The following equation of state was obtained

$$P = RT\sum_{k=1}^{5}\frac{Q_k}{V_k},$$

$$\ln|Q_k| = q_{-2}^{(k)}T^{-2} + q_{-1}^{(k)}T^{-1} + q_0^{(k)}T^0 + q_e^{(k)}\ln T,$$

$$Q_2,\ Q_4 < 0;\ Q_3,\ Q_5 > 0;\ Q_1 = 1,$$

which describes the results of the above-mentioned experiments in the ranges 0.16-126 bar and 780-2170°K. Table 4 shows values of the coefficients of the equation; using this equation and the methods of thermodynamics, we calculated the thermodynamic properties of cesium vapor (Tables 5 and 6). These properties are presented in greater detail, with less spacing between values, in [10]. The readings of entropy and enthalpy begin with the condensation phase at 0°K. The saturation vapor pressure was computed by the same equation used by Nikanorov [11] to generalize the results of many experiments:

$$\ln P = 9.4374 - \frac{8.913}{\tau} - 0.4686\ln\tau,$$

$$[P] = \text{atm},\quad \tau = T/1000,\quad [T] = K.$$

There are presently several published tables of the thermodynamic properties of Cs vapor calculated by the method of mixing its monatomic and diatomic components. The tables in [12] were calculated for a pressure of 20 bar but did not consider the imperfect nature of the components. Thus, the values for density and (especially) heat capacity turned out to be understated. In the tables in [1], a correction was introduced for the imperfect nature of only the monatomic component. However, these calculations were also lacking [13] in that the heat capacity of the vapor was not tabulated.

In Vargaftik's handbook [14], the nonideality of the components of Cs vapor was again not considered, so that the tables are limited to a pressure of 10 bar. The tables

TABLE 2. Empirical PVT Values for Potassium

T, °K	1423	1532	1622	1722	1836	1916	2075
P, bar	12,51	16,15	18,10	20,6	23,7	60,8	72,4
V, m³/kg	0,201	0,173	0,165	0,155	0,145	0,0468	0,0443

TABLE 3. Empirical P_s–T_s Values for Potassium

P_s, bar	T_s, °K	P_s, bar	T_s, °K	P_s, bar	T_s, °K
1,15	1038	6,83	1292	26,1	1578
1,36	1064	7,6	1313	27,3	1586
1,98	1110	7,8	1316	33,3	1640
2,32	1130	9,1	1346	36,1	1660
4,19	1214	14,1	1434	38,8	1682
4,87	1234	15,0	1446	42,9	1712
5,74	1265	24,5	1561	51,2	1667
6,32	1278	25,2	1570	52,5	1773

calculated in [5, 6] on the basis of PVT experiments are more reliable, but they embrace only a small range of the pertinent experiments.

The tables in this article differ from the others by the fact that they are based on experiments on the PVT and speed of sound in cesium vapors embracing a broad range of states. They therefore cover a broader region and are more reliable. They can be supplemented by the tables in [14], which consider the ionization of the monatomic component to 3000°K.

It would be of interest to obtain empirical data for cesium in the liquid phase at high temperatures and pressures.

Until recently, the only reliable empirical data available for liquid cesium was for parameters up to 200°C [15].

The available data on the PVT of liquid cesium at higher temperatures (from 600 to 2200-2500°C), obtained by the radioactive method in [16] and [17], can be regarded only as approximate. The divergence between these sets of data reaches 4% for density and 50% for compressibility.

The physics department at the MAI, together with the I. V. Kurchatov Institute of Atomic Energy, has obtained empirical PVT data for liquid cesium at temperatures from 500 to 1000°K and pressures up to 1000 bar. The measurements were made by the dilatometric method. The error of the resulting data does not exceed 0.2% with respect to density. On the basis of this data, we formulated an equation of state of liquid cesium in the investigated range of parameters, which was then used to compute detailed tables of PVT properties, isothermal compressibility, thermal expansion, and the pressure coefficient. Liquid rubidium and sodium were also studied as part of the same investigation. The experimental data and the equations of state and tables obtained from this data were published in [18-20].

NOTATION

P, pressure; V, specific volume; T, temperature; P_S, T_S, saturation pressure and temperature; R, universal gas constant; i, specific enthalpy; s, specific entropy; c_p and c_v, specific heats at constant pressure and volume, respectively; a, speed of sound; z, compressibility factor; C_k and $q_i^{(k)}$, coefficients in the equation of state.

TABLE 4. Value of $q_i^{(k)}$ Coefficients of Equation of State of Cesium

Coefficient	Q_1	Q_2, m³/kg	Q_3, (m³/kg)²	Q_4, (m³/kg)³	Q_5, (m³/kg)⁴
$q_{-2}\cdot 10^{-6}$	0	+0,34701±0,00004	+11,666±0,0002	−8,914±0,003	0
$q_{-1}\cdot 10^{-4}$	0	+0,26587±0,00004	−3,67347±0,0002	+1,329±0,003	0
q_0	0	+0,15294±0,00004	+168,34±0,0002	+56,87±0,003	−23,7±0,05
q_e	0	−0,92704±0,00004	−21,607±0,0002	−10,29±0,003	0

TABLE 5. Thermodynamic Properties of Saturated Cesium Vapor

T, °K	P, bar	V, m³/kg	i, kJ/kg	S, kJ/kg·deg	c_p, kJ/kg·K	c_p/c_v	a, m/sec	z
950	1,096	0,4870	711,2	1,479	0,2917	1,606	284,6	0,9170
1000	1,711	0,3303	714,2	1,458	0,2965	1,624	289,9	0,9036
1050	2,557	0,2287	717,2	1,439	0,2982	1,644	295,1	0,8903
1100	3,680	0,1640	720,2	1,423	0,2984	1,665	300,0	0,8771
1150	5,126	0,1212	723,2	1,408	0,2993	1,690	304,6	0,8638
1200	6,940	0,09196	726,0	1,395	0,3026	1,718	308,8	0,8502
1250	9,164	0,07134	728,7	1,384	0,3102	1,751	312,2	0,8359
1300	11,83	0,05641	731,2	1,374	0,3228	1,788	314,7	0,8210
1350	14,99	0,04336	733,3	1,365	0,3409	1,831	316,2	0,8052
1400	18,66	0,03701	735,2	1,356	0,3643	1,883	316,8	0,7883
1450	22,86	0,03056	736,7	1,349	0,3929	1,947	316,5	0,7701
1500	27,61	0,02550	737,8	1,342	0,4276	2,031	315,4	0,7505
1550	32,94	0,02146	738,4	1,336	0,4705	2,147	313,3	0,7289
1600	38,84	0,01817	738,1	1,331	0,5274	2,315	310,3	0,7049
1650	45,32	0,01543	736,5	1,326	0,6138	2,585	306,0	0,6774
1700	52,38	0,01307	732,8	1,321	0,7785	3,106	299,6	0,6442
1750	60,03	0,01091	724,2	1,315	1,341	4,824	288,7	0,5984

TABLE 6. Thermodynamic Properties of Superheated Cesium Vapor

T, °K	V, m³/kg	i, kJ/kg	s, kJ/kg·deg	c_p, kJ/kg·deg	c_p/c_v	a, m/sec	z
			$P = 1$ bar				
950	0,5489	713,3	1,486	0,2841	1,603	286,1	0,9236
1000	0,5886	726,5	1,498	0,2538	1,606	298,7	0,9408
1100	0,6626	749,1	1,519	0,2131	1,618	321,5	0,9628
1200	0,7321	768,7	1,535	0,1918	1,628	341,0	0,9752
1300	0,7991	786,8	1,549	0,1805	1,634	358,2	0,9826
1400	0,8647	804,0	1,561	0,1741	1,635	373,7	0,9873
1500	0,9293	820,7	1,573	0,1704	1,635	387,9	0,9904
1600	0,9936	837,1	1,583	0,1683	1,633	401,2	0,9925
1700	1,057	853,4	1,593	0,1672	1,630	413,8	0,9940
1800	1,121	869,6	1,602	0,1667	1,625	425,7	0,9952
1900	1,184	885,8	1,611	0,1670	1,619	436,9	0,9960
2000	1,247	902,0	1,619	0,1677	1,611	447,4	0,9967
			$P = 10$ bar				
1300	0,06885	739,6	1,387	0,2988	1,735	320,6	0,8466
1400	0,07732	766,9	1,405	0,2590	1,707	343,1	0,8828
1500	0,08523	790,8	1,419	0,2320	1,700	363,8	0,9083
1600	0,09278	812,6	1,432	0,2143	1,694	382,1	0,9270
1700	0,1001	832,9	1,444	0,2025	1,685	398,5	0,9408
1800	0,1072	852,2	1,454	0,1945	1,674	413,1	0,9516
1900	0,1141	870,9	1,464	0,1891	1,662	426,5	0,9598
2000	0,1209	889,1	1,472	0,1855	1,648	438,7	0,9662
			$P = 20$ bar				
1450	0,03636	747,2	1,360	0,3281	1,833	325,9	0,8016
1500	0,03867	762,3	1,369	0,2886	1,792	338,9	0,8242
1600	0,04293	788,4	1,383	0,2501	1,773	362,4	0,8577
1700	0,04696	811,9	1,396	0,2309	1,762	382,6	0,8830
1800	0,0508	833,9	1,407	0,2186	1,744	400,1	0,9029
1900	0,05461	854,8	1,417	0,2098	1,723	415,5	0,9188
2000	0,05828	874,9	1,426	0,2034	1,701	429,2	0,9315
			$P = 40$ bar				
1650	0,01898	755,7	1,338	0,3760	2,086	327,3	0,7344
1700	0,02027	772,2	1,345	0,3026	1,9960	345,1	0,7624
1800	0,02259	799,0	1,358	0,2557	1,945	372,8	0,8025
1900	0,02476	823,3	1,368	0,2413	1,901	393,7	0,8333
2000	0,02683	846,5	1,378	0,2331	1,850	410,9	0,8585

TABLE 6

T, °K	v, m^3/kg	i, kJ /kg	s, kJ/kg·deg	c_p kJ/kg·deg	c_p/c_v	a, m/sec	z
			$P = 60$ bar				
1750	0,01083	730,5	1,315	1,3144	4,750	294,7	0,5992
1800	0,01263	757,4	1,326	0,4352	2,563	327,2	0,6730
1900	0,01457	790,5	1,339	0,2860	2,241	367,2	0,7354
2000	0,01620	817,1	1,349	0,2614	2,110	391,2	0,7771
			$P = 80$ bar				
1900	0,00826	729,8	1,312	1,534	3,668	300,8	0,5661
1950	0,00971	763,8	1,322	0,4413	3,136	343,5	0,6360
2000	0,01056	782,5	1,327	0,3391	2,737	365,7	0,6753
2050	0,01130	796,7	1,333	0,3044	2,535	379,9	0,7097
			$P = 85$ bar				
1950	0,00838	745,7	1,315	0,7381	4,396	323,9	0,5839
1975	0,00898	760,3	1,319	0,4908	3,469	342,7	0,6179
2000	0,00945	771,2	1,322	0,3976	3,080	356,1	0,6419
2025	0,00986	780,5	1,325	0,3572	2,899	366,2	0,6614
2050	0,01007	787,6	1,328	0,3314	2,789	373,4	0,6802
			$P = 90$ bar				
2000	0,00834	756,5	1,317	0,5491	3,856	342,4	0,5999
2025	0,00882	768,5	1,320	0,4329	3,361	356,7	0,6268
2050	0,00923	778,4	1,323	0,3881	3,168	367,2	0,6481
			$P = 95$ bar				
2000	0,00694	729,4	1,310	1,738	9,220	316,7	0,5270
2025	0,00779	743,7	1,315	0,5249	3,929	349,3	0,5912
2050	0,00827	765,8	1,318	0,4627	3,601	358,1	0,6124
			$P = 100$ bar				
2050	0,00725	748,5	1,313	0,7209	4,985	344,6	0,5655

Note. The values of i and s of the condensation phase at °K were taken for the beginning of the entropy and enthalpy readings.

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