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

2. DEVELOPMENT OF THERMODYNAMIC FUNCTION TABLES

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Based on experimental data on thermal properties, we have constructed tables of thermodynamic functions for superheated potassium vapor, and these include the values of the specific volume v , enthalpy h , entropy s , isobaric C_p and isochorous C_v heat capacities, speed of sound A , coefficient of compressibility Z , and they encompass areas of parameters related to pressure $P = 0.1-10.0$ MPa and temperature $T = 1075-2150$ K.

In order to calculate the tables of thermodynamic functions, we used a method proposed in [1-3], which had been used successfully by the authors to describe the properties of a number of gases. In accordance with this method, to generalize the experimental data of the PvT relationships of the potassium gas phase we chose an empirical equation of state of the following form:

$$Z = 1 + \sum_{i=1}^{\alpha} \sum_{j=0}^{\gamma} b_{ij} \frac{\omega^i}{\tau^j}, \quad (1)$$

which may formally be interpreted as a portion of the known virial expansion [4], where $\omega = \rho/\rho_{cr}$ and $\tau = T/T_{cr}$ respectively represent the critical points of density and temperature, referred to the parameters. The constants b_{ij} were determined by the method of least squares. The linear system of normal equations derived out of the conditions of the minimum quadratic functional was solved by the method of singular expansion. The set of thermal-property data provided the basis for the construction of a set of

TABLE 1. Coefficients b_{ij} for Equation of State (1)

i	j				
	1	2	3	4	5
0	-0,67220	1,85940	-0,60309	-0,23054	-0,052217
1	-0,89153	1,83340	-0,77899	-0,27837	-0,061728
2	-0,26319	1,78050	-0,98964	-0,33459	-0,072810
3	0,08680	1,68850	-1,2422	-0,40079	-0,085726
4	0,08753	1,54090	-1,5461	-0,47882	-0,10079
5	-0,19345	1,32130	-1,9130	-0,57096	-0,11839
6	-0,46735	1,02000	-2,3582	-0,67999	-0,13895
7	-0,26365	0,65103	-2,9009	-0,80938	-0,16303
8	0,55070	0,28305	-3,5653	-0,96342	-0,19126
9	-0,17398	0,09825	-4,3819	-1,14750	-0,22444

TABLE 2. Comparison of Calculations with Respect to Cesium Vapor on the Basis of Specific Volume v , %

T, K	P, MPa						
	0,1	1,0	2,0	3,0	5,0	10,0	13,0
1100	0,10	—	—	—	—	—	—
1300	-0,01	-0,30	—	—	—	—	—
1500	-0,04	-0,13	-0,13	—	—	—	—
1800	0	-0,09	—	0,40	0,42	—	—
2000	-0,08	-0,08	-0,05	0,13	0,48	—	—
2500	-0,06	-0,30	-0,60	-0,76	-1,00	-1,10	0,45

TABLE 3. Mean-Square Error in Estimate of Thermodynamic Functions for Superheated Potassium Vapor in %

T, K	ΔH	ΔS	ΔC_p	ΔC_v	ΔA	ΔZ
$P=0,1 MPa$						
1100	0,81	0,33	27	34	4,2	0,76
1200	0,26	0,10	11	15	2,2	0,22
1300	0,09	0,03	4,3	6,0	0,95	0,07
1400	0,03	0,01	1,7	2,5	0,40	0,04
1500	0,02	0,005	0,67	1,0	0,18	0,02
1600	0,01	0,004	0,21	0,34	0,07	0,02
1700	0,01	0,004	0,13	0,11	0,02	0,01
1800	0,009	0,003	0,21	0,28	0,05	0,004
1900	0,007	0,003	0,25	0,39	0,08	0,003
2000	0,006	0,003	0,25	0,44	0,10	0,005
2150	0,009	0,004	0,23	0,45	0,12	0,009
$P=1,0 MPa$						
1400	0,24	0,11	8,2	12	2,2	0,09
1500	0,06	0,03	4,1	6,4	1,2	0,09
1600	0,09	0,03	1,4	2,7	0,60	0,09
1700	0,10	0,03	0,74	1,0	0,26	0,06
1800	0,08	0,03	1,6	2,4	0,42	0,02
1900	0,06	0,03	2,1	3,5	0,70	0,02
2000	0,06	0,03	2,3	4,1	0,94	0,04
2150	0,10	0,04	2,1	4,3	1,2	0,08
$P=2,0 MPa$						
1600	0,11	0,03	4,3	6,1	1,1	0,07
1700	0,15	0,05	2,2	3,1	0,57	0,04
1800	0,13	0,05	2,9	4,5	0,75	0,04
1900	0,11	0,05	3,7	6,5	1,3	0,03
2000	0,13	0,06	4,1	7,8	1,8	0,05
2150	0,21	0,09	3,9	8,5	2,4	0,15
$P=3,0 MPa$						
1700	0,18	0,07	4,2	5,9	0,92	0,05
1800	0,16	0,07	4,3	6,7	1,0	0,10
1900	0,16	0,06	5,2	9,4	1,8	0,09
2000	0,21	0,08	5,7	11	2,7	0,05
2150	0,33	0,14	5,5	13	3,6	0,20
$P=5,0 MPa$						
1800	0,29	0,10	9,1	12	1,7	0,18
1900	0,22	0,08	9,4	16	2,9	0,16
2000	0,36	0,13	9,5	19	4,5	0,07
2150	0,61	0,26	8,7	21	6,4	0,29
$P=7,0 MPa$						
1925	0,31	0,12	18	26	4,8	0,12
2000	0,45	0,18	15	29	6,8	0,09
2150	0,90	0,38	13	31	10	0,39
$P=9,0 MPa$						
2025	0,54	0,20	22	44	13	0,27
2100	0,96	0,35	18	43	15	0,01
2150	1,2	0,46	16	43	17	0,30
$P=10,0 MPa$						
2100	1,1	0,34	16	52	23	0,65
2150	1,3	0,48	16	51	24	0,41

TABLE 4. Comparison of Computational Results with Respect to Speed of Sound in Superheated Potassium Vapor against Experimental Data [13, 14]

T, K	P, MPa	A, m·sec ⁻¹		A, %	A, m·sec ⁻¹ calc. [15]
		expt.	calculated		
1090	0,111	571,5	564,9	1,2	555,7
1112	0,113	576,6	574,9	0,30	569,8
1136	0,116	588,9	585,5	0,58	580,1
1157	0,115	599,2	595,5	0,63	590,0
1172	0,117	605,6	601,9	0,61	596,2
1187	0,116	612,3	608,7	0,59	603,2
1211	0,115	623,0	619,4	0,57	613,5
1149	0,114	599,2	592,1	1,2	586,4
1229	0,114	629,5	627,1	0,39	621,0

TABLE 5. Comparing Computational Results with Respect to the Isobaric Heat Capacity of Superheated Potassium Vapor against Experimental Data [12]

T, K	P, MPa	C _p , kJ/(kg·K)		C _p , %	C _p , kJ/(kg·K) [15]
		experiment	calculated		
1095	0,095	0,955	0,995	4,0	0,967
1096	0,095	0,976	0,991	1,5	0,964
1092	0,088	0,938	0,969	3,2	0,952
1091	0,088	0,942	0,973	3,2	0,954
1100	0,096	1,005	0,979	-2,7	0,958
1095	0,089	0,921	0,963	4,3	9,948
1096	0,092	0,942	0,975	3,3	0,955
1095	0,095	0,976	0,995	1,9	0,967

TABLE 6. Comparison of Computational Results with Respect to the Specific Volume of the Superheated Potassium Vapor against Experimental Data [16]

T, K	P, MPa	v, m ³ ·kg ⁻¹		Deviation, Δv, %	v, m ³ ·kg ⁻¹ calc. [15]
		experiment	calculated		
1423	1,251	0,201	0,2037	1,3	0,205
1532	1,615	0,173	0,1712	-1,1	0,172
1622	1,810	0,165	0,1639	-0,7	0,165
1722	2,060	0,155	0,1542	-0,5	0,155
1836	2,370	1,145	0,1437	-0,9	0,145
1916	6,080	0,0468	0,04981	6,0	0,0490
2075	7,240	0,0443	0,04561	2,9	0,0446

equations such as (1), distinguished by the number of constants b_{ij} and an approximation error calculated on the basis of the following formula:

$$\sigma = \sqrt{\frac{\sum_{h=1}^n (1 - \frac{th}{Z_h} \frac{ex}{Z_h})^2}{n - m}}$$

To calculate the thermal functions we subsequently utilized each of the selected equations of state satisfying $\sigma < \sigma_{ex}$

In calculating the thermodynamic properties, in addition to the PvT data derived from [5], we made use of the data from [6]. By varying i from 4 to 11 and by varying j from 3 to 10, we obtained 64 equations of state in the form of (1) with an approximation error of $\sigma = 0.45-0.58\%$. For the true value of the unknown thermodynamic function we adopted the quantity derived by averaging over all the equations of state being worked on here. Thus, the value of the thermodynamic function x (x represents entropy, enthalpy, heat capacity, etc.) is calculated from all of the various equations of state identically well approximating the PvT data. The derived values of x are averaged: $\langle x \rangle = \frac{1}{n} \sum_{i=1}^n x_i$, where n is the number of variants of the equation of state. Table 1 shows the coefficients of b_{ij} for one of the equations used here. Calculation yields values of x closest to the tabulated values of $\langle x \rangle$. Calculation of the thermodynamic properties of potassium vapor from equations of state (1) was accomplished with known thermodynamic relationships

TABLE 7. Thermodynamic Properties of Superheated Potassium Vapor

T, K	$v, m^3 \cdot kg$	$H, kJ/(kg \cdot K)$	$S, kJ/(kg \cdot K)$	$C_p, kJ/(kg \cdot K)$	$C_v, kJ/(kg \cdot K)$	$A, m \cdot sec^{-1}$	Z
$P=0,1 \text{ MPa}$							
1100	2,225	2813	4,828	0,9980	0,6563	573,3	0,9513
1200	2,477	2898	4,855	0,7353	0,4647	618,5	0,9708
1300	2,710	2965	4,890	0,6346	0,3906	657,4	0,9805
1400	2,935	2026	4,926	0,5898	0,3582	690,3	0,9858
1500	3,155	3084	4,961	0,5664	0,3414	719,6	0,9891
1600	3,373	3140	4,995	0,5558	0,3346	745,2	0,9913
1700	3,589	3195	5,026	0,5496	0,3309	769,4	0,9928
1800	3,804	3250	5,057	0,5460	0,3288	792,4	0,9939
1900	4,019	3304	5,085	0,5440	0,3279	814,4	0,9947
2000	4,233	3359	5,113	0,5432	0,3279	835,5	0,9953
2150	4,554	3440	5,152	0,5440	0,3294	865,5	0,9960
$P=1,0 \text{ MPa}$							
1400	0,2571	2873	4,463	1,114	0,7085	602,7	0,8635
1500	0,2856	2973	4,483	0,8901	0,5446	648,7	0,8953
1600	0,3116	3055	4,508	0,7626	0,4625	687,4	0,9159
1700	0,3362	3127	4,536	0,6901	0,4162	721,0	0,9301
1800	0,3599	3194	4,563	0,6456	0,3881	751,1	0,9404
1900	0,3831	3257	4,590	0,6170	0,3704	778,6	0,9481
2000	0,4058	3317	4,617	0,5982	0,3590	803,8	0,9541
2150	0,4393	3406	4,655	0,5812	0,3495	838,5	0,9608
$P=2,0 \text{ MPa}$							
1500	0,1283	2860	4,344	1,216	0,7478	5900	0,8046
1600	0,1430	2968	4,361	0,9563	0,5884	635,3	0,8407
1700	0,1566	3057	4,385	0,8279	0,4999	674,9	0,8662
1800	0,1694	3135	4,410	0,7437	0,4464	710,2	0,8849
1900	0,1817	3207	4,436	0,6894	0,4122	742,2	0,8992
2000	0,1936	3274	4,462	0,6529	0,3897	771,4	0,9104
2150	0,2110	3369	4,500	0,6187	0,3593	810,7	0,9232
$P=3,0 \text{ MPa}$							
1625	0,09059	2920	4,277	1,068	0,6560	603,9	0,7864
1700	0,09762	2995	4,293	0,9361	0,5696	635,6	0,8101
1800	0,1065	3082	4,316	0,8223	0,4951	674,3	0,8349
1900	0,1150	3161	4,342	0,7487	0,4474	709,7	0,8542
2000	0,1233	3233	4,367	0,6989	0,4157	742,1	0,8696
2150	0,1353	3334	4,405	0,6511	0,3863	785,6	0,8876
$P=5,0 \text{ MPa}$							
1800	0,05739	2992	4,190	0,9497	0,5692	614,6	0,7497
1900	0,06276	3081	4,215	0,8356	0,4990	656,6	0,7767
2000	0,06789	3161	4,240	0,7652	0,4533	695,0	0,7982
2150	0,07532	3270	4,279	0,6994	0,4107	746,3	0,8238
$P=7,0 \text{ MPa}$							
1925	0,04168	3029	4,129	0,9589	0,5262	626,8	0,7128
2000	0,04473	3097	4,150	0,8473	0,4798	664,5	0,7363
2150	0,05031	3215	4,190	0,7408	0,4248	726,8	0,7703
$P=9,0 \text{ MPa}$							
2025	0,03227	3040	4,085	1,145	0,5043	674,0	0,6744
2100	0,03508	3115	4,108	0,9096	0,4575	716,5	0,7069
2150	0,03670	3159	4,122	0,8362	0,7225	740,0	0,7225
$P=10,0 \text{ MPa}$							
2100	0,03007	3072	4,078	1,152	0,4757	753,3	0,6734
2150	0,03185	3125	4,093	0,9634	0,4475	774,2	0,6966

[7, 8]. The values of the thermodynamic functions in an ideal gas state for potassium vapors were calculated with thermodynamic potentials taken from a handbook [9].

To evaluate the computation reliability of the programs developed, we undertook a comparison of the calculated thermodynamic properties of superheated cesium vapor against the recommended standard data [10, 11]. Here we employed the same experimental PvT data as in [10]. The results of the comparison with respect to specific volume are shown in Table 2.

As we can see from Table 2, the greatest deviations are encountered in the area of high temperatures and pressures where the number of PvT data is low and the experimental error is the greatest (up to 1%). In this connection, it might be assumed that

this computational method [1-3] satisfactorily describes the PvT surface and that it can be used to describe the properties of potassium vapor.

The mean-square error for the thermodynamic functions in this range of parameters is shown in Table 3. From this we can see that with insignificant scattering of the Z values there exists a significant deviation in the speed of sound and particularly in heat capacity. The greatest scatter is encountered at the edges of the area being studied.

To evaluate the reliability of the tabulated values for the thermodynamic properties we undertook a comparison of the computational results against the experimental data on acoustic and caloric properties (Tables 4 and 5).

It follows from Table 4 that the speed of sound measured in [13, 14] has been reproduced in our studies with an accuracy of 0.3-0.6%, and the magnitude of the mean-square error for A in this interval of parameters amounts to 4.8-2.2% (see Table 3). Table 4 also shows that the speed of sound for these points, obtained in [15] on the basis of calculations, and that this value is lower by 1.2-2.7% than the one experimentally measured.

Comparison of the calculations with the isobaric heat capacity of potassium vapor, as measured in [12], is shown in Table 5. The experimental accuracy, as estimated by the authors of [12], does not exceed 3%. The divergence between experiment and calculation amounts to 2.7-5.8%. Table 5 also shows the values of C_p , obtained for these points in [15], with the deviation of these values from the measurement results falling within an interval of 4.7-1.5%. It should be noted that the calculations in [13] yield systematically exaggerated values for isobaric heat capacity in comparison to experiment, in a range of 4-14%.

Table 6 shows a comparison of the specific volume against experimental data from [16], which were not included in the compilation of the equation of state. We can see from Table 6 that the maximum experimental error reaches 6% for $P > 6$ MPa. Estimate of the accuracy of specific volume for the temperatures and pressures of the experiment in [16] can be found in [15] (the right-hand column of Table 6). The accuracy of the last two points, in the opinion of the authors [15], does not exceed 7%, while for the remaining points it does not exceed 2%.

Thus, results from the analysis and comparison against experimental and theoretical published data [10-18] shows that the error in the coefficient of compressibility does not exceed 1%, and only at a temperature of $T > 1800$ K and $P > 2$ MPa does the divergence from [14] reach 1.5%. In terms of enthalpy, the error amounts to 1% over the entire studied range of temperatures at pressures below 2 MPa. At pressures of 5 MPa the deviation from calculations [15] rises to 2%. Near the saturation line the divergence with respect to entropy reaches 2-3%, becoming smaller on transition to the high-temperature region. As was to be expected, the greatest deviation is found in the isobaric heat capacity, i.e., 10-15%, near the saturation line, and with increasing distance from that line to the region of superheated vapor the error diminishes to 5-10%. In terms of the speed of sound the error amounts to 1-2% at pressures below 2 MPa. With higher pressure values the deviations rise to 3%, diminishing to 0.5 at $P \geq 5$ MPa. In the calculations from [17] for pressures of 0.1-1.5 MPa we encounter an unvalidated large correction factor to account for the fact that the situation is not ideal, and the accuracy of this factor is estimated at 50%.

The tables of the thermodynamic properties for the superheated potassium vapor presented here (Table 7) are based on massive experimental PvT data and presently serve as the only data for this extensive interval of parameters of state.

NOTATION

P, pressure; T, temperature; v, specific volume; H, enthalpy; S, entropy; C_p and C_v , isobaric and isochorous heat capacities; A, speed of sound; Z, compressibility; $\tau = T/T_{cr}$ and $\omega = \rho/\rho_{cr}$, reduced temperature and density; T_{cr} and ρ_{cr} , temperature and density at critical points; b_{ij} , coefficients in equation of state; Z_c^{th} and Z_c^{ex} , theoretical and experimental values for the coefficient of compressibility at the k-th point; σ , approximation error; σ_{ex} , error in experimental data.

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DETERMINING THE HEAT-TRANSFER CONSTANTS OF AN ORTHOTROPIC LAYER

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We propose a method for the calculation of the principal coefficients of the heat-conduction sensor of a flat orthotropic layer, based on results from a nonsteady experiment.

Methods have been proposed in [1, 2] to determine the heat-transfer parameters of anisotropic materials without destruction of their integrity. The object of the study in this case can only be a massive body which can be assumed to be semibounded from the standpoint of heat. In the following we discuss the possibility of determining the thermophysical characteristics of anisotropic materials in the form of black sheets or of coatings on metal structures.

Let us examine an orthotropic layer in an initial uniform temperature field. Let one of its boundary surfaces be forcibly maintained at a constant temperature, while the other surface is insulated against heat, with the exception of a rectangular area that is acted upon by a source of heat arbitrarily distributed over the surface. Let us introduce into this examination the coordinate system (x, y, z), connected to the orthotropy axes, as is shown in Fig. 1. The temperature field $t(x, y, z, \tau)$ for the layer under these conditions will serve as the solution for a boundary-value problem of the form:

$$\lambda_x \frac{\partial^2 t}{\partial x^2} + \lambda_y \frac{\partial^2 t}{\partial y^2} + \lambda_z \frac{\partial^2 t}{\partial z^2} - c\rho \frac{\partial t}{\partial \tau} = 0, \quad (1)$$

$$t(x, y, z, 0) = 0, \quad (2)$$

$$t(x, y, 0, \tau) = 0, \quad (3)$$

$$\lambda_z \frac{\partial t(x, y, \delta, \tau)}{\partial z} = \begin{cases} q(x, y, \tau), & x, y \in S, \\ 0, & x, y \notin S. \end{cases} \quad (4)$$

The function $t(x, y, z, \tau)$ tends toward zero at infinity along the coordinates (x, y) together with the first derivatives.