New Reference Data for Thermodynamical and Transport Properties of Potassium Vapor[1]

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The theoretical calculations of potassium vapor thermodynamical and transport properties on the base of rigorous conditions from nonperfect chemical reacting gases statistical thermodynamics and transport phenomena in dilute gases kinetic theory are fulfilled. In these calculations the spectroscopic and quantum chemical data on the two potassium atoms interaction are used. The parameters, which described the multiparticle contributions to thermophysical properties, are estimated from some experimental thermophysical data. The calculation values of density, heat capacity, sonic velocity, viscosity and heat conductivity are compared with measuring results.

KEY WORDS: experimental thermophysical data; kinetic theory; quantum chemical data; spectroscopic data; statistical thermodynamics; theoretical calculations; two atoms interaction.

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1. INTRODUCTION

At present the sufficiently vast experimental material about thermophysical properties of potassium vapor is accumulated: there are the experimental data about density [1–6], heat capacity at constant pressure [7], sound velocity [8], viscosity [9–12] and heat conductivity [13–16]. On the other hand, there are too highly accurate experimental spectroscopic data about rovibronic levels of K_2 dimers, which allow to describe two potassium atoms interaction in the ground electronic states ^2S ($X\,^1\Sigma_g^+$ [17,18] and $a\,^3\Sigma_u^+$ [19]) and in the excited states ^2S – ^2P [20,21]. As well there are a number of quantum chemical results (for example, [22]). These data allow to define reliably interaction potentials $\Phi_2^{(\mathrm{a})}(r)$ of two potassium atoms K in different electronic states α.

On this base it may be calculated theoretically the second group integral $b_2(T)$, which define in essential manner the thermodynamical behavior of considering substance, and potassium atoms average cross sections $\overline{Q}_{11}^{(l,s)} \equiv \mathrm{ps}\ {}^2\Omega_{11}^{(l,s)*}$, which determine the decisive contribution to its transfer coefficients. The accuracy of initial spectroscopic and quantum chemical data define practically the precision of similar calculations results. The considerably precision my be exceed the accuracy of this thermophysical properties direct measurements results.

For a strong theoretical calculation of potassium vapors thermodynamical and transport properties on the base of rigorous conditions from nonperfect chemical reacting gases statistical thermodynamics and transport phenomena in dilute gases kinetic theory and for the comparison of these calculations results with experimental data it is necessary the senior group integrals $b_j(T)$ (j>2), described the contribution of number j = 3, 4 and

more atoms interaction to thermodynamical properties, and average cross section $\overline{Q}_{12}^{(l,s)}$ and $\overline{Q}_{22}^{(l,s)}$, described the contribution of atom – diatomics (j = 3) and two diatomics (j = 4) collisions. The precision evaluations of those values for potassium vapor are impossible, but their contribution in this substance properties is sufficient small.

To used for these values the simple approximations and rough estimations, one can build the semiempirical correlations, contained a few of fit (free) parameters, and on this base composed the reference tables, which described with high accuracy the all multitude of experimental data (if these data are in concordance) and have the correct asymptotic behavior by low densities.

The creation of these correlations and reference data is the subject of present work.

2. THERMODYNAMICAL PROPERTIES

The semiempirical equation of state for potassium vapor, where atoms K interaction lead to dimers K_2 formation and, generally, another binding complexes K_j, is based on one approach of statistical thermodynamics of nonperfect chemical reacting gases, which known as the basic atoms method. The all details of this approach are described in [23].

Calculation result for second group integral $b_2(T)$ based on the experimental spectroscopic and quantum chemical computation data is presented in Table I. By T<2000 K the $b_2(T)$ evaluation error is less then 0.3% ; its main reason is dissociation energy of K_2 dimer in the $X^1\Sigma_g^+$ state uncertainty. By T≤2500 K the error increase to 0.6% owing to inaccuracy in data that described interaction potentials of exited atoms. For the comparison it is showed in Table I the contribution $b_2^{(0)}$ only the ground

electronic states of interacting atoms to b_2. Temperature dependencies for senior group integrals $b_j(T)$ (j = 3 and 4) include at two free parameters, which were estimated by the least square method by means of exact "low–temperature" experimental data [3] and "high–temperature" data [6] joint treatment. The experimental data [1, 2] are too rough, and then they were not used; data [4, 5, 7, 8] were used only for results control.

Table I. The second group integral and average collision cross sections

T, K	$b_2^{(0)}$, $m^3 \cdot kmol^{-1}$	b_2, $m^3 \cdot kmol^{-1}$	$\overline{Q}_{11}^{(2,2)}/p$, A^2	$\overline{Q}_{12}^{(1,1)}/p$, A^2	A_{12}	B_{12}
800	41.280	41.280	32.03	63.3	1.055	2.108
1000	9.719	9.719	29.53	58.3	1.065	2.179
1200	3.812	3.812	27.75	54.4	1.06	2.15
1400	1.982	1.983	26.32	51.4	1.05	2.10
1600	1.220	1.221	25.10	48.6	1.05	2.02
1800	0.836	0.838	24.03	46.7	1.04	1.97
2000	0.615	0.619	23.06	45.0	1.04	1.92
2200	0.476	0.482	—	—	—	—
2400	0.383	0.390	—	—	—	—

These results are presented in Table II. In this table for each experiment are shown the author's error estimation Δ, the measuring root–mean–square (r. m. s.) deviation from calculated values σ, as well as the two moments of deviations partition function $P(\delta) = dN/d\delta$ ($dN(\delta)$ — the experimental "points" number, which deviations are from δ to $\delta + d\delta$): the shift $s = \overline{d}$ and the width $w = \left[\overline{\left(d - \overline{d}\right)^2}\right]^{1/2}$. If the systematic divergences

amount the experimental data are absent and the correlation model is adequate, then for each experiment $s = 0$ and $w = \sigma$. However it is obvious from Table II, that there are in considered case the marked divergences.

Table II. The comparison of experimental data with thermodynamical properties calculation results

Ref.	Property	Author's error estimation, %	R.m.s. deviation, %	Deviations distribution	
				Shift, %	Width, %
3	Density	0.25—0.35	0.37	–0.15	0.4
6	Density	0.6—1.1	0.60	+0.46	0.3
4	Density	0.5—1.0	3.2	+0.07	3.3
5	Density	—	3.0	+1.4	2.7
7	Heat capacity	3	11	+11	2.0
8	Sonic velocity	0.5	0.56	–0.33	0.2

The values of parameters and their errors estimations, the tables of thermodynamical properties of potassium vapor in region $700 \leq T \leq 2500$ K and $0.01 \leq p \leq 10$ MPa, the tables of errors estimations and comparison with other tables [24, 25] — are published in [23]. Note here only two important circumstances:

i. The suggested semiempirical equation of state contain only 4 free parameters (the equation of state [25], described the same region of temperatures and pressures, include 50 parameters);

ii. The "spectroscopic" second group integral from Table I exactly (practically without the error) correspond to most reliable experimental data [3, 8].

3. TRANSPORT COEFFICIENTS

In the region of temperatures ($700 \le T \le 1900$ K) and pressures ($10^{-5} \le p \le 0.2$ Mpa), where are contained the experimental data [9 — 16], the potassium vapor consist only from monomers K (mole fraction $x_1 \ddagger 0.9$) and dimers K_2, and this system may be considered as the binary reacting ideal gas mixture. The composition of this mixture is defined by chemical equilibrium equation $x_1^2/x_2 = K_p(T)/p$, $x_2 = 1 - x_1$. The equilibrium constant K_p is evaluated from spectroscopic data, as the second group integral, with error less then 0.3%.

For the theoretical calculation the viscosity η and heat conductivity λ coefficients it is used the well–known correlations [26, 27]. The considered procedure was applied earlier for lithium and sodium vapors in [28], where the model features and the errors master sources are described in detail. Note that by low densities (or pressures) $x_1 \to 1$, and the correlations for reacting mixture transport coefficients η and λ are turned into the corresponding formulae for monatomic gas viscosity η_1 and heat conductivity λ_1:

$$\lim_{p\to 0}\eta = \eta_1 = \frac{5}{16}\frac{\sqrt{\pi m k T}}{\overline{Q}_{11}^{(2,2)}} \; ; \qquad \lim_{p\to 0}\lambda = \lambda_1 = \frac{75}{64}\frac{\sqrt{\pi k T / m}}{\overline{Q}_{11}^{(2,2)}} k \, . \qquad (1)$$

The evaluation of potassium atoms collision cross sections $\overline{Q}_{11}^{(2,2)}$ was carried out as in [28]. The results are shown in Table I. These error is conditioned mainly by the potential curves repulsive “branches” uncertainty and don’t exceed 2–3%. The theoretical evaluation method of atom–molecule collision cross sections $\overline{Q}_{12}^{(l,s)}$ is described in [28]. The calculation results are shown also in Table I. These error is more higher because of

atom–molecule interaction potential estimation uncertainty and approximate method employment for account of molecules nonspherical form: its value is 20%. (The values A_{12} and B_{12} in Table I are the certain dimensionless combinations of $\overline{Q}_{12}^{(l,s)}$, which are used for gas mixtures transport coefficients calculations [26]). The choice of molecules cross section $\overline{Q}_{22}^{(2,2)}$ value practically does not influence on the calculation results of h and l . The value $\overline{Q}_{22}^{(2,2)}/\pi$ was taken equal 60 Å^2 as for a hard sphere with diameter $\sigma=2r_e$ (r_e is the equilibrium interatomic distance in molecule). The contributions of atoms K and molecules K_2 exited electronic states by $T\leq2000$ K to considered properties are negligible.

The error of calculated viscosity and heat conductivity values may be estimated from 3 – 4% for $x_2<0.001$ (monatomic gas) to 6 – 7% by $x_2\approx0.1$.

The comparison of theoretical calculations and measurements results is demonstrated in Table III. The concordance of calculated properties and experimental data [12, 16] is excellent; for data [9, 10, 15] it is quite good; for [11, 14] it is may regard as acceptable. Only the data [13] aren't agree neither with the calculation results, nor with other experimental data. One can see also the marked systematic divergences amount the other experimental data. After all, it is necessary to note the systematic character of calculation results deviations from most of experiments: both η and λ calculated values are underrated.

In order to find out the cause of these divergences, it is useful to estimate the atom – atom and atom –molecule collisions cross section values from experimental dependencies $\eta(T,p)$ and $\lambda(T,p)$ and to compare the obtained estimations with quantities from Table I, which were used in theoretical calculations of these dependencies. In [29] for this pur-

pose the theoretical calculated functions $\overline{Q}_{11}^{(2,2)}(T)$ and $\overline{Q}_{12}^{(1,1)}(T)$ in the correlations for $\eta(T,p)$ and $\lambda(T,p)$ evaluations for lithium and sodium vapors were replaced by products $q_1\overline{Q}_{11}^{(2,2)}(T)$ and $q_2\overline{Q}_{12}^{(1,1)}(T)$; the factors q_1 and q_2 were estimated by the least–square method from experimental data. In this work the same procedure was doing for experiments [9 – 16]. One can expect, that in consequence of (1) and owing to high accuracy of the $\overline{Q}_{11}^{(2,2)}(T)$ theoretical calculation the q_1 estimations for all experiments will be found nearly 1 with the straggling in limits 0.95 – 1.05, while the q_2 estimation can differ from 1 systematically and highly essentially. However one can see from Table III, that the treatment of all experiments, excepted [12] and [16], lead to $q_1<1$, and the difference this value for works [10, 11, 13, 14] from 1 markly exceed the summary error of theoretical calculation and measuring. One can assume, that in these experiments any additional systematic errors of the same nature are presented, which their authors aren't taken into consideration.

Table III. The comparison of experimental data with transport properties calculation results

Ref.	Property	Author's error estimation, %	R.m.s. deviation, %	Deviations distribution		q_1	q_2
				Shift, %	Width, %		
9	Viscosity	3	6	+5	2	0.95	0.96
10	Viscosity	2.5	5	+4	2	0.90	1.28
11	Viscosity	3	9	+8	1	0.92	0.81
12	Viscosity	—	5	+3	2	1.00	0.79

13	Heat conductivity	24	31	+30	10	0.91	0.41
14	Heat conductivity	7	13	+11	5	0.93	0.75
15	Heat conductivity	5	6	+5	3	0.95	0.95
16	Heat conductivity	6	7	0	7	1.02	0.98

One can came to following conclusions.

i. The reliable reference data tables of potassium vapor viscosity and heat conductivity by $700 \leq T \leq 2000$ K and $p \leq p_s(T)$ it ought to calculate by using the cross section values from Table I with correction factors $q_1 = 1.00 \pm 0.03$, $q_2 = 0.90 \pm 0.15$.

ii. The same reference data tables [30], which are calculated only on the base of direct treatment of experimental data [10, 14, 15], are suggested apparently the overrate values of these properties for potassium vapor, at least for monatomic vapor (1).

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