

First principles study of the high temperature partition function and heat capacity of the OH⁻ anion [†]

Marcin Buchowiecki^{*†}

Abstract

First principles study of the partition function and heat capacity of OH⁻ anion is conducted at high temperatures (2000K-10,000K). Firstly, with the quantum chemical *ab initio* methods (RASSCF with CASPT2 correction) were used to calculate potential energy curves of the ground and excited electronic states; the energy points were fitted to analytical representation of the curves. Secondly, the statistical thermodynamics calculations with the classical method with the quantum Wigner-Kirkwood correction were performed to obtain partition function and heat capacity.

Thermochemical tables and datasets usually give quantities up to 6000K (sometimes even more) and often are not reliable at the highest temperatures, it is shown that in particular electronic excited states could be missing. Partition function is compared with the only available Barklem and Collet dataset. Discrepancies between heat capacity data (given in NIST-JANAF and Burcat databases) are pointed out - the inclusion of excited electronic states is crucial.

1 Introduction

There is some number of thermochemical tables and datasets such as widely known NIST-JANAF tables [1], NASA polynomials [2] and Burcat thermodynamic database [3] where the high temperature heat capacities can be found. For partition functions there is HITRAN [4] database and databases created for astrophysical applications - ExoMol [5] and Barklem and Collet dataset [6] or for plasma science [7].

The data for the common and typical diatomic molecules are usually reliable unless temperatures are not extremely high [8]; example of such molecule is carbon monoxide [9]. For weakly bounded molecules (Na₂), radicals (NH) or

^{*}corresponding author

[†]Wielkopolska St. 15, Szczecin, Poland

ions (H₂⁺) discrepancies between various data can be significant (and growing with temperature) [10, 11, 12]

Especially important at high temperatures is the inclusion of the electronic excited states in the partition function which for diatomic molecules can be numerous. Below 6000K it is usually sufficient to include electronic states dissociating to the lowest energy channel. The available data are not always accompanied by information which excited states were taken into account for example NIST-JANAF has document [13] which specifies which electronic states were included (those tables are based on quite old data) or ExoMol provides bibliography for each molecule. In general, it is not always known what is exactly included in partition function or heat capacity or it is known that some potential energy curves (PECs) are missing.

Good example of that incompleteness is the hydroxyl anion OH⁻, the document describing the NIST-JANAF values [13] specifies that only the ground electronic state is taken into account in heat capacity, it is easily to guess that at 6000K such approach is not sufficient. The NIST-JANAF heat capacities of OH⁻ anion were not even straightforwardly calculated but obtained by correction from the isoelectronic HF molecule. The heat capacities are also given in Burcat’s “Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion” which, as a newer compilation, is expected to be superior. For the partition function the only data for comparison are in Barklem and Collet (BC) compilation.

The calculated partition function and heat capacity are based on PECs which can be used in the classical approach with quantum corrections (as is done in the present study) or in quantum-spectroscopic approach to calculate ro-vibrational energy levels. Whatever PEC based approach is adopted, it is difficult to find appropriate bibliography; especially excited electronic PECs are often not reported. According to my knowledge, there are no databases of ground and excited PECs in contrast to existing spectroscopic databases.

The publications reporting PECs rarely give convenient functional representations of the curves, even if so, the excited states are usually not included in the study. Usually reported are plots of curves without even energies to which one can fit analytical expressions or compare his or her own results. Those are the problems for high temperature research.

The focus of most PEC studies are the spectroscopic constants by means of which various PECs are compared. However for high temperature research the overall quality of PEC is important and comparing only vibrational frequency ω (describes only vicinity of curves minimum) and dissociation energy D_e and anharmonicity constant x_e (providing general description of curve) is not satisfactory because curves often differs at the region of intermediate bond lengths as in Ref.[11] and as will be shown in the present study for OH⁻. At high temperature quality of the whole curve is important and thus having analytical representation is the most convenient.

In case of OH⁻ anion, the relatively recent studies of PECs are few. Ref.[14] gives the analytical PECs calculated with symmetry adapted cluster-configuration interaction (SAC-CI) method and aug-cc-pVTZ basis set, the shape and the

number of excited states are not in agreement with the more recent studies. Ref. [15] calculates all the curves except the repulsive one (analytical form not given) with the lowest energy dissociation limit with multireference configuration interaction (MRCI) method and V6Z basis set. Ref. [16] report all the curves (again analytical forms not given) with complete active space self-consistent field (CASSCF) approach, followed by the internally contracted MRCI and MRCI+Q techniques (as implemented in MOLPRO) and gives also molecular terms of all the PECs correlating with three lowest dissociation limits.

The rest of article is organized as follows: Section 2 described the used quantum chemistry and statistical thermodynamics methods, Section 3 presents results with discussion and finally Section 4 concludes the study.

2 Methods

Potential energy curves ¹Σ⁺, ³Π, ¹Π, and ³Σ⁺ (which dissociate to O⁻(²P_u) and H(²S_g)) were calculated with multiconfigurational methods implemented in OpenMolcas [17] which is package aimed, among others, at excited states. The Restricted Active Space Self-Consistent Field (RASSCF) method [18] was followed by perturbational multi-state CASPT2 method [19] to add dynamical correlation lacking in the RASSCF method.

The basis set used was ANO-L-VQZP and there were the following active (RAS1) orbitals: 8 of *a*₁ symmetry, 2 of *b*₂ symmetry, 1 of *a*₂ symmetry, and 2 of *b*₁ symmetry.

Ab initio calculations of the PECs even for relatively simple OH⁻ molecule is not straightforward, as can be seen articles mentioned in Introduction, and appropriate methods have to be chosen[20, 21]; in particular intruder states may effect calculations. Even the simplest molecular anion was discussed relatively recently [20].

Classical method with quantum correction of integration over the phase space. The all-states partition function will be calculated with the expression which takes into account all the interactions between atoms (bound, metastable, and scattering) [22, 23, 24, 25]:

$$Q_{int}^{WK3} = \frac{g(ele)}{2\sqrt{\pi}} \left(\frac{2\mu}{\beta} \right)^{3/2} \int_0^\infty [\exp(-\beta V(r))wk3(r) - \exp(-\beta V(\infty))]r^2 dr, \quad (1)$$

where $\beta = 1/(k_B T)$ is the inverse temperature, V is the potential energy function of the molecule, $g(ele)$ is the multiplicity of a given electronic state, $V(\infty)$ the energy of dissociated atoms, and $wk3(r)$ the correcting Wigner-Kirkwood

factor[26, 27]:

$$\begin{aligned}
 wk3(r) = 1 - \frac{\beta^3}{24\mu} (V')^2 + \\
 + \frac{\beta^4}{5760\mu^2} \left(\beta^2 (V')^4 - 8\beta (V')^2 r^{-2} d[r^2(V')]/dr + 12(r^{-2} d[r^2(V')]/dr)^2 \right) + \\
 + \frac{\beta^5}{16\mu^3} \left[\frac{V'''}{840} + \frac{(V'')^2}{140r^2} + \frac{\beta}{726} (V'')^3 + \frac{\beta}{180} \frac{V'(V'')^2}{r} + \frac{\beta}{945} \frac{(V')^3}{r^3} - \right. \\
 \left. - \frac{\beta^2}{720} (V')^2 (V'')^2 - \frac{\beta^2}{6480} \frac{(V')^4}{r^2} - \frac{\beta^3}{2160} \frac{(V')^5}{r} + \frac{\beta^4}{25920} (V')^6 \right]. \quad (2)
 \end{aligned}$$

If negative contribution of scattering states is to be excluded, it can be done approximately by simple cut off of the part of PEC over the dissociation energy in Eq.1 [28, 24, 22, 12]; that method is also a simple way of detecting influence of scattering states. At most temperatures the effect of scattering states is negligible and exclusion of this effect is convention in thermochemistry[29].

The heat capacity at constant pressure is calculated as a numerical derivative from internal partition function $Q(\beta)$:

$$C_p = \beta^2 \frac{d^2 \ln Q(\beta)}{d\beta^2} R + (5/2)R, \quad (3)$$

where $R = 8.3145 J/(mol \cdot K)$.

Except for heat capacities atomic units are used in this study.

3 Results and Discussion

3.1 Quantum chemistry

The energy points for each electronic state calculated in the present study and fitted curves alongside with the ground state of Ref. [14] are given in Fig.1. It is seen, as already mentioned, that often the curves (here two ¹Σ curves) differ in the range of intermediate internuclear distances and still vibrational frequency can be for both curves the same; it will have effect on calculated quantities. The curves in Fig. 1 after fitting were shifted upwards so that the minimum of the ground curve had energy zero.

The hump in the repulsive PEC can be due to avoided crossing, so that smoothening it probably desirable.

The electronic ground state (¹Σ; according to Jiang *et al.*[14]) is given as

$$\begin{aligned}
 V_{1\Sigma J}(r) = 0.18338 - 0.18338e^{-2.31515(r-1.81962)}(0.590412(r-1.81962)^3 + \\
 + 1.28003(r-1.81962)^2 + 2.31515(r-1.81962) + 1). \quad (4)
 \end{aligned}$$

The ground state fitted to calculated points, in the functional form given in Ref. [30], is

$$V_{1\Sigma}(r) = \frac{e^{-2.62477r} \left(\frac{5.21549}{r} + 1 \right) + e^{-1.29711r} \left(\frac{1}{r} - 1.4229r \right)}{1 - 0.227428e^{-r} \left(\frac{r^2}{3} + r + 1 \right)} + 0.186982 \quad (5)$$

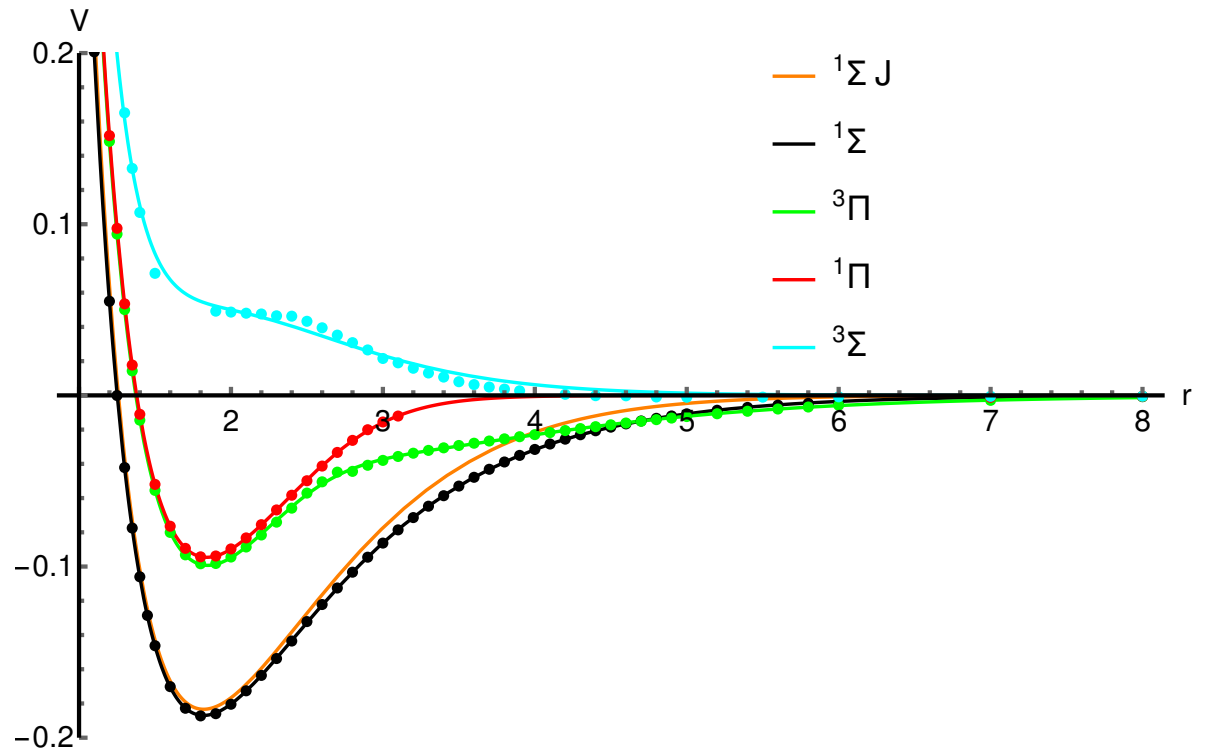


Figure 1: Potential energy curves of the OH^- anion: the ground state $^1\Sigma$, and three excited states: $^3\Pi$, $^1\Pi$, and $^3\Sigma$. The ground state of Ref. [14] is also shown ($^1\Sigma J$).

The excited states are given in the analogous functional form, but with more free parameters to obtain enough flexibility. They are as follows, ³Π state

$$V_{3\Pi}(r) = \frac{e^{-2.05551r} \left(\frac{19.2005}{r} - 29.2719 \right) + e^{-0.940982r} \left(\frac{5.24103}{r} - 0.36864r \right)}{0.563172e^{-r} (-4.47836r^2 + 4.36231r + 1) + 1} + 0.186982, \quad (6)$$

¹Π state

$$V_{1\Pi}(r) = \frac{e^{-3.3267r} \left(112.973 + \frac{53.9949}{r} \right) + e^{-3.32684r} \left(-67.2466r - \frac{81.9248}{r} \right)}{1 - 1.44943e^{-r} (2.21394r^2 - 3.67549r + 1)} + 0.186982, \quad (7)$$

and the repulsive ³Σ state

$$V_{3\Sigma}(r) = e^{-1.97872r} \left(11746.8 - \frac{59.0562}{r} \right) + e^{-1.97961r} \left(\frac{84.2026}{r} - 11777.5 \right) + 0.186982. \quad (8)$$

In Fig. 1 some points in the ¹Π and ³Σ curves are missing, they were omitted due to erratic behavior, some attempted changes in the active space do not resulted in desired smoothness.

Note also that the depth of potential well of ³Π curve (and also ¹Π) is more shallow in Refs. [15] and [16] than in Ref. [14] (all those studies used different methods). In the attempt to resolve I have used Psi4 package [31] for the ³Π state and potential well depth estimated with EOM-CC3 or CCSD(T) (aug-cc-pVQZ basis set) confirmed the present results; only few points were calculated and those curves are not shown because behavior of energy points was more erratic than OpenMolcas results. This shows the need of high quality research of excited states of even simple molecules.

Since I was not able to definitively resolve the problem with the ³Π and ¹Π states I have used simple division by two to decrease well depths and then the curves are approximately, by only possible visual inspection, as the ones reported in Refs. [15, 16].

3.2 Statistical thermodynamics

In table 1 the partition functions based on the ground electronic state are compared. There are two rigid-rotor harmonic oscillator values, one based on the experimental frequency $3738.44\text{cm}^{-1} = 0.017033586a.u.$ and the equilibrium bond length $1.8225a.u.$ [32] (RRHO exp.) and the second based on the Jiang *et al.* frequency $3782.915\text{cm}^{-1} = 0.0172362291$ and the equilibrium bond length $1.81962a.u.$ [14] (RRHO J). In Ref. [16] experimental and theoretical spectroscopic constants from various sources are tabulated and significant discrepancies are reported not only for the excited electronic states but also a ground state; note also that NIST and Herzberg give frequency of 3700cm^{-1} . Those discrepancies (which effects increase with temperature) and the nature of the present research which is based on PEC function (see Eq. 1) is the reason that the spectroscopic constants are not of interest here. The difference between RRHO exp. and RRHO J partition functions is not very significant, it is 1% at 6000K.

The next columns of Table 1 give values based on the $V_{1\Sigma J}$ PEC [14] on Eq. 1 (Q J) and with excluded negative part (Q NE J) which approximately excludes scattering interaction of atoms; it can be seen that the effect of scattering is negligible at the temperatures under consideration (especially in the light of the overall discrepancy of presented values). Last two columns (Q and Q NE) are based on the ground curve of obtained in this study. At 6000K the difference between partition functions based on the *Jiang et al.* and the present PEC is around 2% - this confirms significant influence of the intermediate bond length region (for the difference in PECs see Figure 1).

In particular RRHO approximation is not adequate at any temperature so that this approximation is not used for heat capacities reported in Table 2. Again the values based on the *Jiang et al.* PEC (C_p J and C_p NE J) and the present PEC (C_p and C_p NE). The difference between the heat capacities based on both PECs is 2.3% at 6000K (more than 2% for internal partition function even if it is not internal quantity but contains common $5R/2$ factor).

Table 2 shows also NIST values which are known to be based only on the ground electronic state [13] and Burcat database values which as systematically higher may include contribution from excited electronic states (this specific information is not given in the database). The present values (as the one based on the other PEC) are between NIST and Burcat values.

Table 3 shows the effect of inclusion of excited states - firstly the two attractive and finally also the repulsive one inclusion of which lowers the partition function value because of negative contribution of the purely repulsive curve. Comparison with the Barklem and Collet [6] results that the only ground electronic state is taken into account, this can be concluded from values at high temperatures (5000K and higher) at which the influence of excited electronic states is pronounced enough.

Note that over 6000K there was no data for comparison and it couldn't be definitively concluded if Burcat data contained excited electronic states. This will be attempted now in Tables 4 and ?? which give heat capacities calculated on ground and excited states. Inspection of values in Table 4 allows to conclude that inclusion of $^3\Pi$ and $^1\Pi$ excited states are not included in the presently obtained form -Burcat values are systematically lower. The inclusion of all excited states (also the repulsive $^3\Sigma$ state) is non-negligible over 6000 K.

Table 5 reports the heat capacities based on potential energy curves of the $^3\Pi$ and $^1\Pi$ states divided by two to qualitatively simulate PECs of lower potential depths than the ones calculated in this study. Below 5000K a good agreement is reached with the Burcat data but discrepancies at higher temperatures suggests that Burcat database do not take excited electronic states in the proper or accurate enough manner.

4 Conclusions

The general conclusion, shown on the example of OH⁻ anion, is that the available heat capacities can be compromised (as concluded for the NIST database)

or uncertain at high temperatures (as concluded for the Burcat database) because of not exact enough inclusion of excited electronic states.

At lower temperatures (below 2000K-3000K) general agreement of various data is relatively good (because of small or negligible influence of excited electronic states).

The present method naturally takes into account all interactions between atoms (bound, metastable, and scattering) but scattering states effect is very small until very high temperatures so that the classical Wigner-Kirkwood corrected method can be safely used (at temperatures high enough for the classical with quantum correction treatment). It is important to remember that scattering states have to be excluded to conform with thermodynamical convention but if all interatomic interactions are to be included the present method is the method of choice.

Finally, the basis of high temperature statistical thermodynamic calculations are the PECs of ground and excited electronic states and reliably calculated curves are needed - this requirement seems to be presently not easily achievable.

5 Keywords

excited electronic states, scattering states, partition function, heat capacity

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Table 1: Internal partition functions of OH⁻ based on ground state PEC. RRHO approximation based on experimental [32] spectroscopic parameters (RRHO exp.), RRHO approximation based on the Jiang *et al.* parameters [14] (RRHO J), values of Eq. 1 and negative contribution excluded (Q J and Q NE J respectively; based on Jiang *et al.* PEC), and the values based on PEC of this study according to Eq. 1 (Q) and with negative contribution excluded (Q NE).

T(K)	RRHO exp.	RRHO J	Q J	Q NE J	Q	Q NE
2000	78.01	77.59	82.606	82.605	83.125	83.125
2500	102.86	102.19	110.05	110.05	110.81	110.81
3000	130.86	129.90	141.42	141.42	142.54	142.54
3500	162.12	160.81	177.16	177.16	178.76	178.76
4000	196.69	194.98	217.55	217.55	219.81	219.81
4500	234.61	232.43	262.88	262.88	266.00	266.00
5000	275.87	273.20	313.44	313.44	317.71	317.71
5500	320.50	317.27	369.54	369.54	375.33	375.34
6000	368.50	364.67	431.52	431.53	439.31	439.32
7000	474.60	469.41	574.39	574.44	588.19	588.23
8000	594.21	587.45	744.40	744.56	767.90	768.04
9000	727.33	718.80	943.20	943.61	981.42	981.77
10,000	873.95	863.46	1171.6	1172.5	1230.7	1231.5

Table 2: Heat capacities of OH⁻ based on ground state PEC. Values calculated from partition function of Eq. 1 and negative contribution excluded (C_p J and C_p NE J respectively; based on Jiang *et al.* PEC), and the values based on PEC of this study according to partition function of Eq. 1 (C_p) and with negative contribution excluded (C_p NE). NIST values (NIST) and Burcat values (Burcat) are shown for comparison.

T(K)	C_p J	C_p NE J	C_p	C_p NE	NIST	Burcat
2500	35.71	35.71	35.84	35.84	35.74	35.92
3000	36.87	36.87	37.03	37.03	36.60	36.96
3500	37.71	37.71	37.92	37.92	37.23	37.85
4000	38.42	38.42	38.71	38.71	37.72	38.70
4500	39.09	39.10	39.49	39.49	38.13	39.60
5000	39.74	39.74	40.29	40.29	38.48	40.60
5500	40.35	40.35	41.08	41.09	38.79	41.74
6000	40.88	40.90	41.83	41.85	39.06	43.04
7000	41.62	41.65	43.02	43.05	-	-
8000	41.76	41.83	43.53	43.58	-	-
9000	41.33	41.43	43.30	43.38	-	-
10,000	40.66	40.59	42.46	42.57	-	-

Table 3: Internal partition functions of OH⁻ based on ground and excited states PECs. Value with negative contribution excluded based on the ground state only (Q NE) is compared with and the values based on ground and two excited states (³Π and ¹Π) with negative contribution excluded (Q g+2e) and with all contributions based on Eq. 1 (Q g+2e) and with all PECs (³Π, ¹Π, and the repulsive ³Σ) included (Q g+2e+rep). Partition functions according to Barklem and Collet (BC) are given for comparison.

T(K)	Q NE	Qg+2e NE	Q g+2e	Q g+2e+rep	BC
2000	83.125	83.126	83.126	83.126	83.238
2500	110.81	110.83	110.83	110.83	-
3000	142.54	142.65	142.65	142.65	143.11
3500	178.76	179.32	179.32	179.32	-
4000	219.81	221.73	221.72	221.72	221.29
4500	266.00	271.24	271.24	271.22	-
5000	317.71	329.86	329.85	329.76	320.69
5500	375.34	400.24	400.21	399.94	-
6000	439.32	485.72	485.63	484.95	445.60
7000	588.23	717.78	717.34	714.37	602.13
8000	768.04	1060.3	1058.9	1049.7	797.75
9000	981.77	1547.5	1543.9	1521.6	1040.3
10,000	1231.5	2208.9	2201.0	2155.4	1337.3

Table 4: Heat capacities with excited electronic states included. The ground state based heat capacity with negative contribution excluded (C_p NE) is compared to heat capacity with two excited states with negative contribution excluded (C_p g+2e NE), heat capacity with two excited states with all contributions (C_p g+2e), and heat capacity with all excited states under consideration including the repulsive one (C_p g+2e+rep). The NIST values (NIST) and Burcat values (Burcat) are also given.

T(K)	C_p NE	C_p g+2e NE	C_p g+2e	C_p g+2e+rep	NIST	Burcat
2500	35.84	35.97	35.97	35.97	35.74	35.92
3000	37.03	37.63	37.63	37.63	36.60	36.96
3500	37.92	39.66	39.66	39.66	37.23	37.85
4000	38.71	42.55	42.54	42.54	37.72	38.70
4500	39.49	46.48	46.47	46.47	38.13	39.60
5000	40.29	51.28	51.24	51.24	38.48	40.60
5500	41.09	56.39	56.33	56.31	38.79	41.74
6000	41.85	61.06	60.96	60.92	39.06	43.04
7000	43.05	66.51	66.31	66.16	-	-
8000	43.58	65.64	65.37	64.90	-	-
9000	43.38	60.62	60.33	59.30	-	-
10,000	42.57	54.34	54.04	52.31	-	-

Table 5: Heat capacities with excited electronic states included. Heat capacity with two excited states with negative contribution excluded (C_p g+2e NE), heat capacity with excited states PECs which lowered energy wells (C_p g+2e V/2), heat capacity with excited states PECs which lowered energy wells and negative contribution excluded (C_p g+2e V/2 NE), and Burcat values (Burcat).

T(K)	C_p g+2e NE	C_p g+2e V/2	C_p g+2e V/2 NE	Burcat
2500	35.97	35.84	35.84	35.92
3000	37.63	37.06	37.06	36.96
3500	39.66	38.06	38.06	37.85
4000	42.55	39.25	39.26	38.70
4500	46.48	40.94	40.96	39.60
5000	51.28	43.33	43.37	40.60
5500	56.39	46.40	46.50	41.74
6000	61.06	49.91	50.09	43.04
7000	66.51	56.56	56.94	-
8000	65.64	60.18	60.74	-
9000	60.62	59.81	60.48	-
10,000	54.34	56.58	57.28	-