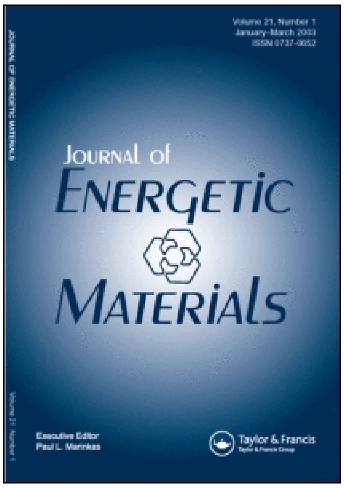

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Theoretical calculations of thermodynamic properties of chlorotetrazoles and nitrotetrazoles

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Theoretical calculations of thermodynamic properties of chlorotetrazoles and nitrotetrazoles

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ABSTRACT

Ab initio molecular orbital method was performed to calculate the enthalpies, heat capacities and entropies of chlorotetrazoles and nitrotetrazoles in the temperature range 100 -1000K. A scaling factor(0.90) for frequencies at HF/6-31G* level are proposed based on comparison of the calculated and the experimental thermodynamic data of 2H-tetrazole. The results show that chlorotetrazoles and nitrotetrazoles have similar thermodynamic properties respectively. Finally the heat capacity-temperature dependence in the form $(a+bT+cT^2)$ are presented by fitting the calculated heat capacity results.

INTRODUCTION

Thermodynamic properties, such as enthalpy, entropy and free energy, are necessary for predicting the direction of a chemical reaction and equilibrium concentration. In designing and synthesizing new type explosives, thermodynamic data are also needed for calculating explosive temperature and heat. Often these data are not known experimentally, especially for those of unstable compounds. At this time one can resort to expensive (sometimes dangerous) experiments to obtain the necessary data or they may calculate them from empirical models such as group additivity methods. Such methods work very well for hydrocarbons, but they often fail for other classes of compounds[1]. On the other hand, ab initio molecular orbital computation can provide the raw material needed for calculation of ideal gas thermodynamic properties at any temperature, based on standard methods of statistical mechanics[2]. In fact, the so called "theoretical thermochemistry" have achieved great success in predicting heat of formation of AH_m molecules[2] and entropies and heat capacities of organosilicon compounds[3,4]. Nowadays more and more papers dealing with theoretical calculations of thermodynamic properties appear in the scientific journals[5-7].

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Recently, there has been widespread interest in tetrazole compounds, due to their various applications in agriculture, medicine and explosives[8]. The thermodynamic data of gaseous tetrazole compounds are limited to heats of formation for some of tetrazole derivatives[9] though the thermodynamic properties of tetrazole were determined[10]. So far as we know, there are no theoretical prediction of thermodynamic properties of tetrazole compounds. In this paper we focus on two kinds of tetrazole derivatives: chlorotetrazoles and nitrotetrazoles for which there are no experimental thermodynamic data available. For a particular substituent, there are, theoretically, five neutral molecules derived from the three parent compounds of tetrazole(i.e: 1H-, 2H- and 5H-tetrazole), namely 1-R-tetrazole, 2-R-tetrazole, 5-R-1H-tetrazole, 5-R-2H-tetrazole and 5-R-5H-tetrazole(R=substituent group, here refers to -Cl and -NO_2). Since the 5H-tetrazole is higher in energy than the 1H- and 2H-isomers by about 80KJ/mol and 90 KJ/mol respectively[11], we have not studied it in this paper. The molecular structures of compounds studied in this paper are displayed in Fig.1. Three types of thermodynamic functions: standard molar enthalpy(H°_{m}), standard molar heat capacity($C^{\circ}_{p,m}$) and standard molar entropy(S°_{m}) are calculated. As there are no experimental results, we hope to compensate for the lack of experimental data by theoretical means.

COMPUTATIONAL METHODS

Enthalpy, heat capacity and entropy were calculated according to the general statistical thermodynamic method[12]. The absolute entropy of the ideal gas at 1 atm can be written

$$S=S_t+S_r+S_v$$

where S_t,S_r and S_v are the translational, rotational and vibrational entropies, respectively, and according to statistical thermodynamics, they follow

$$S_t=R\ln(f_t e/N_0)+1.5R$$

where f_t is the transitional molecular partition function which depends on the mass of the molecule and temperature, N_0 is Avogadro constant and R is the gas constant.

$$Sr=R\ln(f_r)+1.5R\text{(for a non-linear molecule)}$$

$$Sr=R\ln(f_r+R)+1.5R\text{(for a linear molecule)}$$

where f_r is the molecular rotational partition function which depends on the mass of the molecule and the optimized molecular geometric configurations and

$$S_v = R\ln(f_v) + U_v/T$$

where f_v is the sum of various harmonic vibrational partition functions and Uv is the sum of various harmonic vibrational energies, both of which depends on all the harmonic vibrational frequencies.

The heat of capacity at 1 atm can be written as

$$Cp = C_t + C_r + C_v + R$$

where C_t,C_r and C_v is the contribution of the translation, rotation and vibration respectively. The last mainly depends on various harmonic frequencies.

Quantum-chemical calculations were performed using Gaussian 92[13] program. Both geometrical optimizations and frequency calculations were carried out at HF/6-31G* [14] level on a Tontru Pentium personal computer in our laboratory. The frequencies used for calculating thermodynamic properties are scaled by 0.90(see below). The calculations of thermodynamic properties were completed using a self-compiled program on the same computer.

RESULTS AND DISCUSSIONS

1 Molecular Geometries and Frequency Scaling

All the optimized molecular geometries for the titled compounds are depicted in Fig.1 and Table 1. All of them belong to Cs point group. The unscaled vibrational frequencies are listed in Table 3. In the following thermodynamical calculations of the thermodynamic properties all the frequencies are scaled by 0.90. As can be seen that the lowest vibrational frequencies of nitrotetrazoles are higher than those of chlorotetrazoles.

The theoretically calculated frequencies, especially at relatively lower theoretical level, are overestimated and they should be scaled by a factor to get close to the experimental results. The scaling factor depends on the theoretical level and varies a little with different compounds. The most-commonly used scaling factor is 0.89 for frequencies at HF/6-31G* level[15]. So far as we know there are no scaling factor for tetrazole compounds. To find the factor suitable for calculating thermodynamic properties of tetrazole compounds, we calculated the thermodynamic functions, with the frequencies scaled with various factors, of 2H-tetrazole for which the experimental gaseous thermodynamic properties have been measured[10]. The maximal absolute deviations(m) and root mean square errors(r) for Cp, S and H at different scaling factors are listed in Table 2. It is clear from the table that for Cp and H the m's and r's reach the smallest at f=0.90 whereas the corresponding errors for S at f=0.90 are a bit larger than those at f=0.89 respectively. In this paper we chose f=0.90 as the scaling factor. At this scaling factor, the maximum absolute errors for Cp, H and S are 0.67J/k/mol, 0.17kJ/mol and 0.89 J/K/mol, respectively, which are a bit superior to the corresponding errors(1.255J/K/ mol) from additivity methods[16].

2 Thermodynamic Properties

The calculated heat capacities, enthalpies and entropies of the titled compounds in the temperature range 100-1000K are listed in Table 4. The heat capacities and temperature dependence in the form a+bT+cT2 are contained in Table 5.

From Table 4 we can see that as the temperature goes up, the difference between the thermodynamic functions of the anions and those of the corresponding neutrals increase. For example, at 400 k the enthalpy of (1) is larger than that of (5) by 0.15kJ/mol while at 1000K the difference is 5.67kJ/mol. This is because the neutrals have more vibrational levels than the anions(see Table 3). Generally speaking, chlorotetrazoles have similar thermodynamic properties, obviously, due to, them being isomers and having similar molecular geometries and electronic structures. The same trends can be found for nitrotetrazoles. As nitrotetrazoles have more vibrational levels than the corresponding chlorotetrazoles and the lowest vibrational frequencies of the former are lower than those of the later, the thermodynamic functions of nitrotetrazoles are larger than those of chlorotetrazoles at any temperature.

The fitting parameters for heat capacity is very similar, except that nitrotetrazoles have larger values than the chlorotetrazoles.

Although we can not make direct comparison between our theoretical results and experimental ones, the relatively small deviation for 2H-tetrazole lead us to believe that our computation results are quite reliable, as chlorotetrazoles and nitrotetrazoles are derivatives of tetrazole. We hope our theoretical results will receive experimental support in the future.

CONCLUSION

We have predicted heat capacities, entropies and enthalpies of chlorotetrazoles and nitrotetrazoles by means of ab initio calculations. The temperature dependence functions of heat capacity are also presented. Tetrazole compounds with the same kind substituent have similar thermodynamic properties. The maximum deviations are thought to be less than 1.0kJ/mol, 1.0J/K/mol and 1.0J/K/mol for H, Cp and S respectively.

REFERENCES

[1] D.A. Dixon and B.E. Smart, Chem. Eng. Commun., 1990, 98, 173

[2] J.A. Pople,B.T.Luke,M.J.Frisch and J.S.Binkley, J.Phys.Chem., 1985, 89, 2198.

[3] G.Z. Ju and W.S.Bian, Thermochimica, Acta, 1990, 167,37.

[4] G.Z. Ju and W.S.Bian, Thermochimica, Acta, 1991, 176,259.

[5] S. Roszak, K. Balasubramanian, Chem. Phys. Lett., 246(1995)20

[6] A. Bauke, D.Yu and D.A. Armstrong, J. Am. Chem. Soc., 119(1997)208.

[7] H. Kudo, M.Hashimoto, K. Yokoyama, C.H. Wu and P.v.R. Schleyer, Thermochimica acta, 299 (1997)113.

[8] R.N. Butler, Adv. Heterocycl. Chem., 21(1977)323.

[9] A.A Kozyro, V.V. Simirsky, A.P. Krasulin, V.M. Sevruk, et al, Z. Fiz. Khim. 64(1990)656.

[10] Kabo G.J., Kozyro A.A., Krasulin A.P., Sevruk V.M. and Ivashkevich L.S., J. Chem. Thermo dynamics, 1993,25,485.

[11] M. W. Wong, R. L. Leung-Toung, C. Wentrup, J.Am.Chem.Soc.,1993, 115, 2465

[12] T.L. Hill,"Introduction to Statistical Thermodynamics", Addision-Wesley Publishing Company, INC, New York,1960

[13] Gaussian 92/DFT, Revision F.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. W. Wong, J. B. Foresman, M. A. Robb, M. Head-Gordon, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J.A.Pople, Gaussian, Inc., Pittsburgh PA, 1993.

[14] W. J. Hahre, L. Radom, P. V. R. Schleyer, J. A. Pople, "Ab Initio Molecular Orbital Theory" , Wiley: New York,1986

[15] J. A. Pople, R. Krishnan, H. B. Schlegel, et al., Int. J. Quantum Chem. Symp., 1981, 15, 2691

[16] S.W.Benson, Pure Appl.Chem.,52(1980)1767.

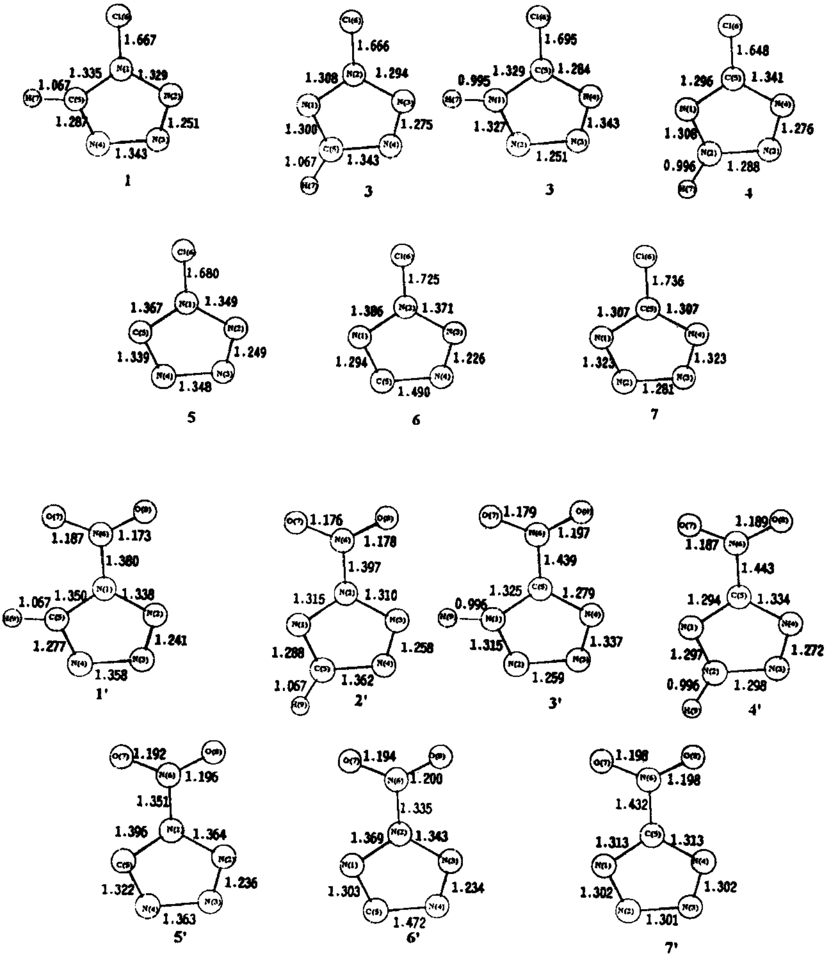

FIGURE 1 Optimized geometries at HF/6-31G* level for the titled compounds(Bond lengths in Å).

TABLE 1 The optimized bond angles for chlorotetrazoles(unit: degree)*

Angle	1	2	3	4	5	6	7
N2N1C5	108.56	100.78	107.48	100.63	114.15	107.14	102.68
N1N2N3	106.10	114.72	106.72	114.40	103.66	109.40	110.22
N2N3N4	111.71	106.02	111.58	106.75	111.98	107.10	110.20
N3N4C5	106.06	106.29	105.26	105.42	110.20	110.52	102.69
N1C5N4	107.60	112.19	108.97	112.80	100.01	104.70	114.21
R2R1C16	121.97	122.38	127.23	123.20	118.46	112.60	122.89
N4C5H7	127.84	124.03	-	-	-	-	-
N2N1H7	-	-	121.72	-	-	-	-
N3N2H7	-	-	-	122.58	-	-	-

*: R1 and R2 represent N1 and N2 in 1 and 5 respectively, N2 and N3 in 2 and 4, or C5 and N4 in 3,4 and 7(see Fig.1)

TABLE 1 Continued

Angle	1'	2'	3'	4'	5'	6'	7'
N1N2N3	105.72	114.60	107.22	114.41	103.75	112.81	110.09
N2N3N4	112.05	105.75	111.22	106.62	112.70	105.58	110.09
N3N4C5	106.39	106.70	104.76	105.08	110.39	111.07	103.19
N4C5N1	107.03	112.15	109.98	113.51	100.21	105.18	113.44
C5N1N2	108.81	100.79	106.81	100.38	112.94	105.38	103.19
N6R1R2	122.97	122.44	127.86	123.53	119.35	121.99	123.28
O7N6R1	114.09	115.13	117.88	116.43	117.48	117.29	118.11
O8N6R1	116.76	115.20	114.58	116.53	117.76	117.73	118.11
H9C5N4	128.42	123.71	-	-	-	-	-
H9N1N2	-	-	123.10	-	-	-	-
H9N2N3	-	-	-	122.56	-	-	-

TABLE 2 The calculated errors of thermodynamic properties for 2H-tetrazole at different scaling factors*

Erros	88	89	90	91	92	93	94
r_{Cp}	1.57	0.95	0.40	0.44	0.99	1.58	2.17
m_{Cp}	2.14	1.40	0.67	0.77	1.25	1.73	2.22
r_H	0.77	0.44	0.12	0.20	0.52	0.82	1.13
m_H	1.15	0.64	0.17	0.34	0.83	1.31	1.79
r_S	1.07	0.42	0.61	1.30	2.01	2.72	3.41
m_S	1.57	0.66	0.89	1.50	2.49	3.48	4.42

*: r denotes the root mean square error.m refers to maximum absolute error.

TABLE 3 The calculated frequencies(cm^{-1}) for the titled compounds(Cs) at HF/6-31G* level*

Compds.	Vibrational frequencies
(1)	198 343 558 693 803 1005 1088 1112 1229 1283 1330 1540 1584 1695 3504
(2)	215 368 573 728 792 1019 1110 1130 1253 1362 1408 1460 1503 1693 3503
(3)	291 345 553 620 793 809 1111 1172 1200 1230 1434 1581 1596 1736 3914
(4)	302 360 557 668 807 838 1126 1164 1291 1329 1435 1502 1612 1727 3911
(5)	175 357 545 651 803 1012 1085 1199 1221 1293 1432 1635
(6)	158 336 503 658 729 830 1003 1060 1139 1176 1589 1756
(7)	297 355 526 814 835 1152 1156 1268 1288 1440 1521 1592
(1′)	97 178 285 511 630 669 790 879 948 1031 1067 1090 1207 1313 1400 1549 1567 1647 1740 1931 3526
(2′)	74 190 302 518 633 697 783 871 950 1034 1063 1125 1228 1376 1441 1485 1543 1605 1745 1944 3508
(3′)	80 252 254 488 594 699 742 817 883 946 1111 1192 1223 1246 1460 1534 1644 1665 1776 1905 3892
(4′)	44 262 268 493 592 715 767 825 902 954 1148 1174 1277 1361 1471 1535 1595 1694 1758 1895 3894
(5′)	71 185 315 531 598 638 785 907 956 962 1105 1146 1286 1363 1474 1599 1716 1840
(6′)	92 104 307 530 595 603 730 813 882 951 1074 1087 1322 1393 1519 1605 1734 1821
(7′)	56 258 280 499 594 772 841 895 957 1174 1190 1215 1384 1400 1530 1649 1671 1827

*; All the frequencies are not scaled.

TABLE 4 The calculated thermodynamic properties for titled compounds*

T(K)	1	2	3	4	5	6	7
H_m° 100	3.55	3.51	3.44	3.43	3.58	3.63	3.44
200	8.26	8.13	8.07	7.97	8.33	8.53	7.92
298	14.33	14.10	14.21	13.98	14.38	14.88	13.65
300	14.47	14.24	14.35	14.12	14.52	15.02	13.78
400	22.33	22.00	22.29	21.93	22.18	23.01	21.05
500	31.67	31.26	31.69	31.20	31.09	32.22	29.59
600	42.21	41.74	42.25	41.66	40.98	42.32	39.15
700	53.67	53.15	53.71	53.03	51.58	53.10	49.48
800	65.85	65.30	65.87	65.12	62.72	64.38	60.38
900	78.60	78.01	78.58	77.77	74.26	76.03	71.73
1000	91.78	91.17	91.71	90.86	86.11	87.96	83.40
$C_{p,m}^\circ$ 100	40.59	39.77	38.60	38.10	41.04	41.98	38.26
200	54.11	53.14	54.32	53.21	54.37	56.72	51.53
298	70.04	69.02	70.98	69.58	69.11	72.50	65.42
300	70.38	69.36	71.31	69.92	69.41	72.80	65.70
400	86.43	85.53	87.15	85.81	83.33	86.51	79.47
500	99.88	99.16	100.26	99.12	94.45	97.01	90.93
600	110.41	109.86	110.51	109.57	102.81	104.78	99.78
700	118.53	118.11	118.40	117.64	108.99	110.51	106.43
800	124.83	124.50	124.52	123.90	113.60	114.78	111.44
900	129.80	129.53	129.35	128.84	117.06	118.00	115.25
1000	133.76	133.55	133.22	132.79	119.72	120.48	118.18
S_m° 100	243.51	242.70	242.20	241.96	243.72	244.62	241.71
200	275.63	274.19	273.63	272.83	276.12	278.03	272.28
298	300.12	298.28	298.38	297.08	300.52	303.62	295.38
300	300.59	298.74	298.86	297.54	300.99	304.10	295.82
400	323.08	320.95	321.60	319.88	322.92	327.00	316.65
500	343.86	341.55	342.51	340.51	342.76	347.49	335.66
600	363.05	360.62	361.73	359.54	360.76	365.90	353.06
700	380.70	378.20	379.38	377.07	377.09	382.50	368.96
800	396.96	394.40	395.61	393.20	391.96	397.55	383.52
900	411.96	409.37	410.57	408.09	405.55	411.26	396.87
1000	425.85	423.23	424.40	421.87	418.03	423.83	409.17

*: $C_{p,m}^\circ$ and S_m° are in $JK^{-1}mol^{-1}$. H_m° in kJ/mol.

TABLE 4 Continued

T(K)	1'	2'	3'	4'	5'	6'	7'
H°_m 100	4.04	4.08	4.02	4.14	4.09	4.22	4.08
200	9.87	9.87	9.87	9.95	9.90	10.21	9.78
298	17.57	17.50	17.66	17.64	17.53	18.05	17.17
300	17.75	17.68	17.84	17.82	17.71	18.24	17.34
400	27.83	27.71	28.01	27.87	27.57	28.30	26.85
500	39.89	39.72	40.12	39.86	39.18	40.08	38.13
600	53.56	53.36	53.81	53.44	52.19	53.21	50.83
700	68.49	68.26	68.73	68.27	66.26	67.37	64.64
800	84.40	84.15	84.62	84.08	81.13	82.32	79.29
900	101.08	100.81	101.26	100.65	96.62	97.86	94.59
1000	118.36	118.08	118.49	117.84	112.57	113.86	110.39
$C^\circ_{p,m}$ 100	49.75	49.46	49.11	49.02	49.48	51.28	48.64
200	67.80	67.25	68.61	67.88	67.57	69.61	65.82
298	89.48	88.87	90.50	89.34	88.18	90.45	85.05
300	89.93	89.32	90.95	89.78	88.60	90.86	85.45
400	111.32	110.78	111.98	110.71	107.97	109.84	104.46
500	129.29	128.87	129.60	128.44	123.73	125.14	120.47
600	143.52	143.20	143.55	142.57	135.87	136.93	133.04
700	154.59	154.35	154.42	153.60	145.07	145.88	142.68
800	163.23	163.04	162.90	162.22	152.05	152.68	150.03
900	170.04	169.90	169.60	169.03	157.38	157.89	155.68
1000	175.47	175.36	174.95	174.47	161.52	161.93	160.07
S°_m 100	257.09	258.30	257.61	261.99	258.66	260.30	259.67
200	296.82	297.72	297.38	301.49	298.22	301.07	298.51
298	327.84	328.50	328.80	332.52	328.98	332.73	328.30
300	328.44	329.10	329.40	333.12	329.57	333.33	328.87
400	357.30	357.79	358.51	361.87	357.79	362.15	356.10
500	384.14	384.53	385.46	388.55	383.65	388.37	381.19
600	409.02	409.34	410.38	413.26	407.33	412.28	404.32
700	432.01	432.29	433.36	436.11	429.00	434.09	425.58
800	453.24	453.49	454.55	457.20	448.84	454.03	445.14
900	472.88	473.10	474.14	476.72	467.07	472.33	463.15
1000	491.08	491.30	492.30	494.82	483.88	489.18	479.79

TABLE 5 The fitting parameters for the heat capacity of the titled compounds1)

Parameters	1	2	3	4	5	6	7
a(JK^{-1}mol^{-1})	18.5511	17.5353	16.9418	16.3155	21.7588	23.0569	19.2511
b(JK^{-1}mol^{-1})(-3)	204.652	204.856	213.004	210.370	188.668	195.374	183.780
-c(JK^{-1}mol^{-1})(-5)	8.93350	8.86340	9.71715	9.41196	9.12344	9.90989	8.50327
S2)	0.98	0.98	0.98	0.98	0.97	0.96	0.97
	1′	2′	3′	4′	5′	6′	7′
a(JK^{-1}mol^{-1})	20.2806	19.8581	20.2129	20.2111	22.5986	24.9078	22.2881
b(JK^{-1}mol^{-1})(-3)	274.022	273.505	277.085	272.720	260.100	259.039	249.237
-c(JK^{-1}mol^{-1})(-5)	11.8677	11.7756	12.2553	11.8435	12.1668	12.2729	11.1418
S	0.98	0.98	0.98	0.98	0.97	0.96	0.98

1) **The temperature range is 100–1000K**

2) **S is the correlation coeffecient**