Thermodynamic properties of vanadium and cobalt argide ions, VAr^+ and $CoAr^+$

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Abstract. The positive ions of 3d metal and argon compounds (metal argide ions, MAr^+) play essential role in the mass spectrometry with argon plasma sources. At the same time their thermodynamical properties are still not sufficiently studied. Rough estimations of the internal partition functions of MAr^+ have been made by Witte and Houk in order to calculate the concentration ratio between metal and metal argide ions in the plasma. In this work we performed more accurate estimations of the internal partition functions for VAr^+ and $CoAr^+$, for which the experimental measurements of molecular constants are available. The thermodynamic functions and equilibrium constant for reaction $M^+ + Ar = MAr^+$ were obtained for the temperatures up to 10^4 K. The molecular constants were used to construct the potential curves for the ground and excited states of the molecules. The one-dimensional Schrodinger equation was solved using the Level code to find the rovibronic levels of the electronic states for the specified potential. Different potential models such as a simple Morse potential and the potential with the long range electrostatic attraction were used for comparison.

There is no data about thermodynamic functions for 3d-metal argide ions in the literature. Meanwhile these complexes are observed in plasma mass spectrometry, when Ar is utilized to generate the plasma. Its thermodynamic properties are essential in order to model processes that proceed in ICP mass spectrometry and to forecast intensity of corresponding ion current in the analysis of mass-spectra, because they can mask traces of heavy admixtures.

Calculation of internal partition function for 3d-metal argide ions is not the trivial task, because of following issues: a) there is small quantity of experimental data about molecular constants of such complexes; b) such complexes have small dissociation energy in comparison with demanded temperatures. The basic source of information for calculating partition function is theoretical quantum mechanical computation of main spectroscopic parameters: R_e (internuclear distance in the minimum of the potential well), D_e (dissociation energy), W_e (vibrational constant, corresponding to degree of curvature in the minimum). Small dissociation energy does not allow using of simple Harmonic Oscillator Rigid Rotator (HORR) approach [1] widely used in calculations of thermodynamic properties of molecules with deep potential well (see e.g. [2]).

In order to calculate vibration-rotational partition function of 3d metal argide ions, their potential curves were considered on the base of available spectroscopic parameters. Two different model potentials were used for this:
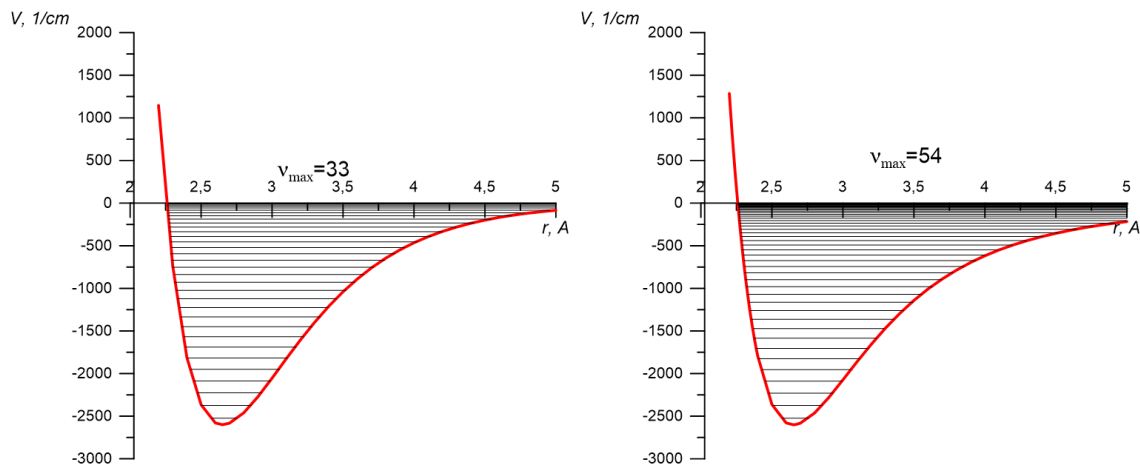
Figure 1. (On the left) $X^5\Sigma^+$ ground state of VAr^+: calculated vibrational levels for the Morse potential.

Figure 2. (On the right) The same as in figure 1 but for the Bellert–Brekenridge potential [3].

(i) Morse potential that normally used to describe covalent bond in the molecule

$$V(r) = D_e \left(1 - e^{-b(r-R_e)}\right)^2. \tag{1}$$

(ii) Long range electrostatic attraction potential, that was listed by Bellert and Breckenridge in their work [3]

$$V(r) = -\frac{\alpha_{\mathrm{Rg}}Z^2}{2r^4} - \frac{C_6}{r^6} - \frac{\alpha_{\mathrm{RgQ}}Z^2}{2r^6} + \frac{B_{\mathrm{Rg}}Z^3}{2r^7} - \frac{\alpha_{\mathrm{RgO}}Z^2}{2r^8} - \frac{C_8}{r^8} - \frac{\gamma Z^4}{24r^8} + Ae^{\mathrm{br}}. \tag{2}$$

Rovibronic energy levels for specified potential were computed using LEVEL 8.2 code [4], which applies numerical algorithms in order to determine the discrete eigenvalues of the radial one-dimensional Schrodinger equation. As the result this code provides the energies of vibrational levels and the coefficients of polynomial for calculating the rovibronic energy levels

$$E_{\nu,J} = G(\nu) + B_\nu[J(J+1)] - D_\nu[J(J+1)]^2 + H_\nu[J(J+1)]^3 + \ldots = \sum_{m=0} K_m(\nu)[J(J+1)]^m. \tag{3}$$

In figures 1 and 2 the potential curves with the calculated vibrational levels are shown. Although both potentials look similar and have the same main spectroscopic parameters, the system described by the Bellert-Breckenridge potential has essentially more vibrational levels than the system described by the Morse potential.

In order to calculate the vibration-rotational partition function of electronic states, the auxiliary Partition Function code was developed. This code reads the output data from LEVEL 8.2 code [4] and computes the partition function taking into account the following conditions.

First as the equations for calculating the rovibronic energies is polynomial of the seventh degree (3), it is essential to check that the level energy increases with the increase of the rotation number J. Analogous inspection must be performed when vibrational number is rising.

The second issue is that the potential energy is given by

$$V_J(r) = V_0(r) + \left(\frac{h}{8\pi^2\mu c}\right) J(J+1)\frac{1}{r^2}. \tag{4}$$
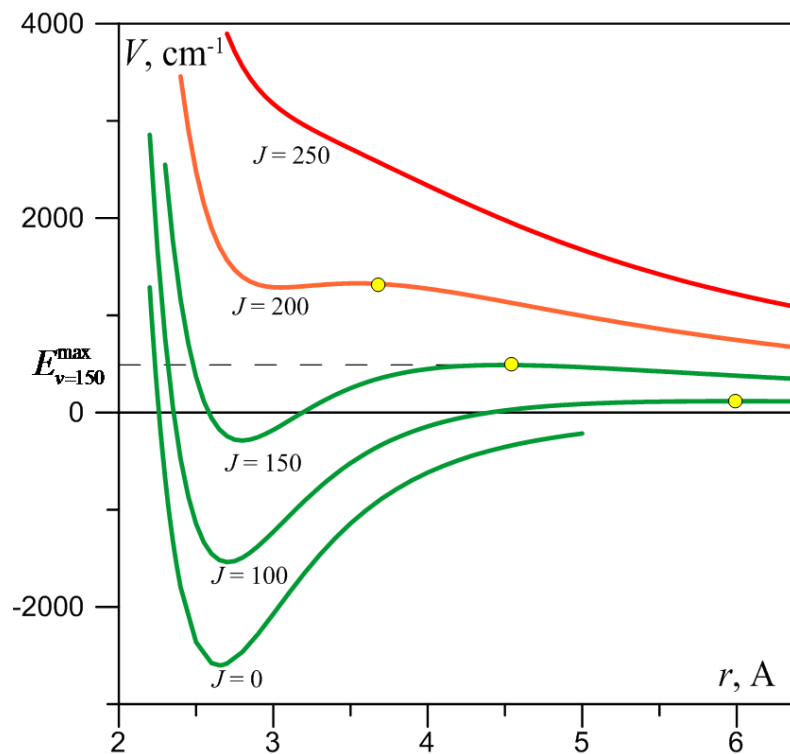
Figure 3. Potential energy depending on the the rotational number J for $X^5\Sigma^+$ ground state of VAr^+. Small yellow circles indicate local maxima.

Due to that with the increase of the rotational number J, first the local maximum appears on the potential curve. At some value of J this maximum disappears together with the general minimum so that the curve becomes monotonic (see figure 3). The Partition Function code controls that the rovibronic level energy calculated by equation (3) is lower than the local maximum energy of the potential for the corresponding rotational number J.

Taking the above restriction into account, the Partition Function code calculates the vibration-rotational partition function of an electronic state using the equation

$$Q_{\mathrm{vib-rot}} = \sum_{v,J} \left[(2J+1) \mathrm{e}^{-(E(v,J)-E(0,0))/k_{\mathrm{B}}T} \right]. \tag{5}$$

In figure 4 the results for the computed vibration-rotational partition function for VAr^+ in the ground electronic state are presented. Different types of potential were probed with the same values of main spectroscopic parameters. Figure 4 shows that two variants of the HORR approach result in large errors. At the same time the difference between the Morse potential and the Bellert-Breckenridge potential (that is more accurate at large distances) does not exceed $5-10\%$ at all temperatures. Therefore the use of Morse potential is acceptable when the given accuracy is sufficient. It should be noted however, that the the Morse potential involves only three parameters, while the Bellert-Breckenridge potential has a more complex equation (see (2)).

Using our Partition Function code we performed calculations of $Q_{\mathrm{vib-rot}}$ for fifteen Ω-states that correlate with spin-orbit components of the VAr^+ ground LS-term $^5D(3d^4)$ and for twelve Ω-states that correlate with spin-orbit components of the $CoAr^+$ ground LS-term $^3F(3d^8)$. Potential curves of the Ω-states were modeled using theoretical data on the relative energies
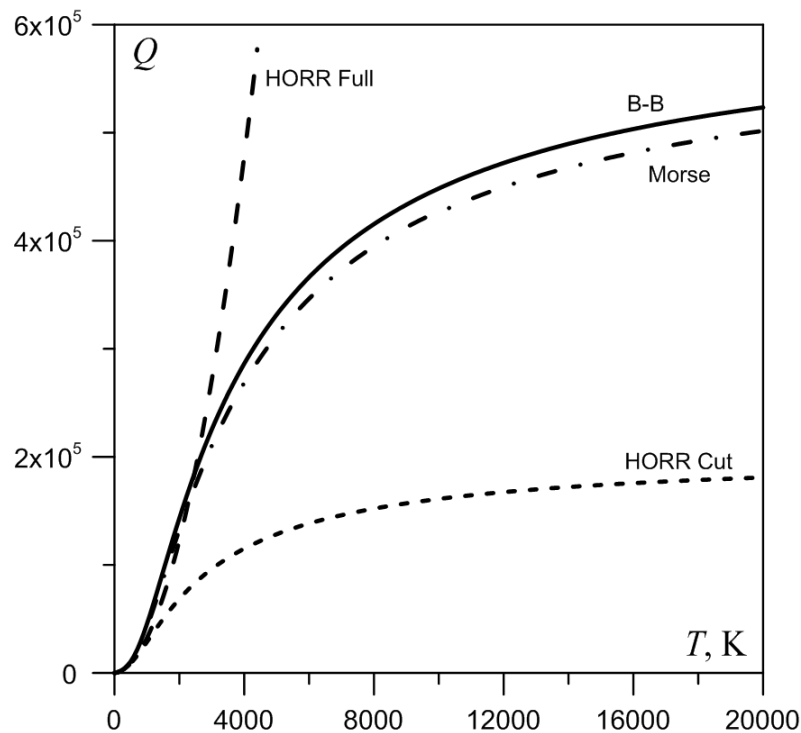
Figure 4. Partition function for VAr^+ ground state obtained using different interatomic potentials: "HORR Full"—Harmonic Oscillator Rigid Rotator approach, "HORR Cut"—the same taking the levels below the dissociation limit, "B-B"—see equation (2), "Morse"—Morse potential (1).

and R_e of ΛS-states from [5] and experimental data on the dissociation energy D_0 and the values of R_e for the ground Ω-state: VAr^+, $\Omega = 0$, $^5\Sigma_0^+$ [3, 6]; $CoAr^+$, $\Omega = 3$, $^3D_3$ [3, 7]. The ΛS-states potentials were described by equation (2) with $Z = 1$ and the electrostatic attraction parameters given in [3]. The spin-orbit interaction in MAr^+ was assumed to be the same as for M^+ ion. Additional calculation details will be presented elsewhere.

At the temperature $T = 10\,000$ K the calculated $Q_{vib-rot}$ values lie in the range of 390 000–460 000 for VAr^+ and 540 000–590 000 for $CoAr^+$. In addition we obtained the values of $Q_{vib-rot}$ for the experimentally observed excited states $^5P_1(3d^44s)$ of VAr^+ [3, 6]; $^3F_4(3d^74s)$ and $^3P_2(3d^74s)$ of $CoAr^+$ [3, 7]. The rounded $Q_{vib-rot}$ values are 296 000, 325 000, and 336 000 for the first, second, and third state, respectively.

The next step was to calculate the values of internal partition function Q_{int} for VAr^+ and $CoAr^+$. In the equation

$$Q_{int} = \sum_{ik} g_{ik} Q_{vib-rot}^{ik} e^{-(E_{ik}-E_{00})/k_B T}, \tag{6}$$

the electronic states of MAr^+ are numbered with a double index ik. The first number indicates the correlation of the MAr^+ electronic state with the i-th electronic state of the M^+ ion. The sum of the statistical weights g_{ik} is equal to g_i.

Substituting $E_{ik} = E_i - D_0^{ik}$ in (6), where E_i is the energy of the i-th electronic level of M^+ and E^{ik}, D_0^{ik} are respectively energy and dissociation energy of the ik-th electronic state of

Table 1. Thermodynamic functions for the vanadium argide positive ion.

Vanadium argide positive ion VAr$^+$						
V$^+$ + Ar = VAr$^+$, $\Delta_r H°(0) = -35.673\,\mathrm{kJ} \times \mathrm{mol}^{-1}$						
T	$C_p°(T)$	$\Phi°(T)$	$S°(T)$	$H°(T) - H°(0)$	$\lg K°(T)$	T
K	$\mathrm{J} \times \mathrm{K}^{-1} \times \mathrm{mol}^{-1}$			$\mathrm{kJ} \times \mathrm{mol}^{-1}$		K
298.150	50.503	225.307	263.468	11.378	2.8325	298.150
300.000	50.634	225.541	263.781	11.471	2.7910	300.000
400.000	53.332	237.071	278.884	16.728	1.1373	400.000
500.000	51.757	246.651	290.659	22.002	0.1711	500.000
600.000	48.690	254.782	299.837	27.031	-0.4574	600.000
700.000	45.145	261.761	307.079	31.724	-0.8992	700.000
800.000	41.604	267.803	312.874	36.060	-1.2288	800.000
900.000	38.346	273.079	317.583	40.055	-1.4868	900.000
1000.000	35.565	277.726	321.474	43.745	-1.6968	1000.000
1500.000	31.774	294.695	334.730	60.048	-2.3825	1500.000
2000.000	27.340	305.739	342.744	74.010	-2.7976	2000.000
2500.000	26.679	313.762	348.736	87.430	-3.0968	2500.000
3000.000	27.301	320.014	353.645	100.895	-3.3313	3000.000
4000.000	29.515	329.476	361.792	129.271	-3.6874	4000.000
5000.000	31.554	336.635	368.608	259.852	-3.9544	5000.000
6000.000	32.899	342.467	374.491	192.143	-4.1682	6000.000
7000.000	33.444	347.418	379.614	225.382	-4.3462	7000.000
8000.000	33.207	351.727	384.073	258.770	-4.4987	8000.000
9000.000	32.254	355.539	387.936	291.557	-4.6323	9000.000
10000.000	30.670	358.953	391.257	323.068	-4.7516	10000.000

$$M = 90.8889$$
$$\Delta_f H°(0) = 1128.800\,\mathrm{kJ} \times \mathrm{mol}^{-1}$$
$$\Delta_f H°(298.15) = 1135.598\,\mathrm{kJ} \times \mathrm{mol}^{-1}$$
$$S°_{\mathrm{nucl}} = 17.682\,\mathrm{J} \times \mathrm{K}^{-1} \times \mathrm{mol}^{-1}$$

$$\Phi°(T) = 486.4169777 + 86.0555922\ln(x) - 0.00847674037x^{-2} + 1.752847549x^{-1}$$
$$-266.23008429x - 193.3549537286x^2 + 1337.70128708283x^3$$
$$(x = T \times 10^{-4}; 298.15 < T < 1500\,\mathrm{K})$$

$$\Phi°(T) = 332.1812428 + 2.170849983\ln(x) + 0.197687156x^{-2} - 7.313112216x^{-1}$$
$$+46.05081337x - 13.66621252x^2 + 1.499948029387x^3$$
$$(x = T \times 10^{-4}; 1500 < T < 10000\,\mathrm{K})$$

MAr$^+$, one can obtain

$$Q_{\mathrm{int}} = \sum_i e^{(-E_i - E_0)/k_{\mathrm{B}}T} \sum_k g_{ik} Q_{\mathrm{vib-rot}}^{ik} e^{(D_0^{ik} - D_0)/k_{\mathrm{B}}T}. \tag{7}$$

This equation allows us to calculate the part of Q_{int} related to the low-lying Ω-states for which the values of $Q_{\mathrm{vib-rot}}^{ik}$ and D_0^{ik} have been obtained above. This part (part 1) is dominant at relatively low temperatures. The other parts of Q_{int} (parts 2, 3, 4) we have determined as the

Table 2. Thermodynamic functions for the cobalt argide positive ion.

T	$C_p^\circ T)$	$\Phi^\circ(T)$	$S^\circ(T)$	$H^\circ(T) - H^\circ(0)$	$\lg K^\circ(T)$	T
K	\multicolumn{3}{c}{$J \times K^{-1} \times mol^{-1}$}	$kJ \times mol^{-1}$		K

T K	$C_p^\circ T)$	$\Phi^\circ(T)$	$S^\circ(T)$	$H^\circ(T) - H^\circ(0)$	$\lg K^\circ(T)$	T K
298.150	43.476	221.948	260.701	11.554	5.0044	298.150
300.000	43.493	222.189	260.790	11.635	4.9503	300.000
400.000	45.103	233.537	273.682	16.057	2.7697	400.000
500.000	46.748	242.627	283.933	20.654	1.4635	500.000
600.000	47.700	250.248	292.553	25.383	0.5949	600.000
700.000	47.842	256.828	299.926	30.167	−0.0235	700.000
800.000	47.248	262.624	306.284	34.927	−0.4859	800.000
900.000	46.057	267.791	311.785	39.597	−0.8450	900.000
1000.000	44.441	272.432	316.557	44.124	−1.1331	1000.000
1100.000	42.585	276.636	320.706	48.477	−1.3702	1100.000
1200.000	40.684	280.465	324.330	52.640	−1.5697	1200.000
1300.000	38.934	283.962	327.516	56.619	−1.7412	1300.000
1400.000	37.536	287.177	330.347	60.438	−1.8908	1400.000
1500.000	36.691	290.142	332.904	64.144	−2.0232	1500.000
2000.000	31.600	302.128	342.612	80.968	−2.5205	2000.000
2500.000	29.238	310.935	349.379	96.108	−2.8635	2500.000
3000.000	28.038	317.794	354.592	110.394	−3.1254	3000.000
4000.000	27.119	328.035	362.500	137.863	−3.5155	4000.000
5000.000	27.065	335.553	368.536	164.911	−3.8038	5000.000
6000.000	27.385	341.475	373.495	192.115	−4.0326	6000.000
7000.000	27.864	346.361	377.751	219.733	−4.2224	7000.000
8000.000	28.371	350.524	381.505	247.853	−4.3848	8000.000
9000.000	28.806	354.156	384.873	276.451	−4.5267	9000.000
10000.000	29.083	357.384	387.924	305.411	−4.6529	10000.000

$$M = 98.895$$
$$\Delta_f H^\circ(0) = 1079.634 \text{ kJ} \times \text{mol}^{-1}$$
$$\Delta_f H^\circ(298.15) = 1086.422 \text{ kJ} \times \text{mol}^{-1}$$
$$S^\circ_{\text{nucl}} = 17.526 \text{ J} \times \text{K}^{-1} \times \text{mol}^{-1}$$

$$\Phi^\circ(T) = 266.324211719 + 12.444517344\ln(x) + 0.00294694886x^{-2} - 0.57372212185x^{-1} + 567.2339024059x - 1936.2937279628x^2 + 2844.79727082856x^3$$
$$(x = T \times 10^{-4}; 298.15 < T < 1500 \text{ K})$$

$$\Phi^\circ(T) = 362.736632729 + 25.698789141\ln(x) + 0.1329649529x^{-2} - 4.3869317212x^{-1} - 3.903259523755x + 3.7869495837x^2 - 0.983104635848x^3$$
$$(x = T \times 10^{-4}; 1500 < T < 10000 \text{ K})$$

contributions of the states that correlate with a) the terms of $3d^{n+1}$ configuration excluding the ground LS-term; b) the terms of $3d^n4s$ configuration; c) the terms of other configurations M^+.

These parts were calculated using the equation

$$Q_{\text{int}} = \sum_i g_i e^{-(E_i - E_0)/k_{\mathrm{B}}T} Q_{\text{vib-rot}}^{\text{av}} e^{(D_0^{\text{av}} - D_0)/k_{\mathrm{B}}T}, \qquad (8)$$

where $Q_{\text{vib-rot}}^{\text{av}}$ and D_0^{av} are approximate average values of $Q_{\text{vib-rot}}^{ik}$ and D_0^{ik}. For the part 2 we have estimated the values of $Q_{\text{vib-rot}}^{\text{av}}$ and D_0^{av} using the values $Q_{\text{vib-rot}}^{ik}$ and D_0^{ik} from the part 1. For the part 3 we have done the same but using the values $Q_{\text{vib-rot}}^{ik}$ and D_0^{ik} for $^5\mathrm{P}_1(3\mathrm{d}^4 4\mathrm{s})$ state of VAr^+, and $^3\Phi_4(3\mathrm{d}^7 4\mathrm{s})$, $^3{}_2(3\mathrm{d}^7 4\mathrm{s})$ states of CoAr^+ (see above). For the part 4 no values of Q_0^{ik} and D_0^{ik} are available, therefore we have accepted the values of $Q_{\text{vib-rot}}^{\text{av}}$ and D_0^{av} as in the part 3. Note, that the part 4 correlates with high terms of M^+ and it constitutes less than 1.1% of Q_{int} even at 10 000 K. The energy levels for V^+ and Co^+ were taken from [8].

Subsequent calculations of thermodynamic functions of VAr^+ and CoAr^+ have been performed using procedures set out in the reference book [9]. The results are shown in tables 1 and 2 which are the standard forms [9].

The concentration ratio of MAr^+ and M^+ at the thermal equilibrium can be calculated by multiplying the tabulated values of $K^\circ(T)$ to the argon pressure in the units of atm. At the room temperature and 1 atm argon pressure, almost all metal ions are associated with argon atoms. If we assume that the thermal equilibrium is achieved on the axis of inductively coupled plasma ion source in a mass spectrometer (which is quite questionable), the concentration ratio $\mathrm{VAr}^+/\mathrm{V}^+$ at 6000 K would be of 68 ppm, and that of $\mathrm{CoAr}^+/\mathrm{Co}^+$ would be of 93 ppm. This is 2 to 3 times more than the values of 31.2 ppm and 31.5 ppm obtained in [10]. We hope that the thermodynamic properties of metal argide ions will be useful for understanding the processes in plasma mass spectrometry.

Acknowledgments

References

[1] Herzberg G 1971 *The Spectra and Structures of Simple Free Radicals: An Introduction to Molecular Spectroscopy* (Mineola, NY: Dover Publications, Inc.)
[2] Osina E L and Gusarov A V 2015 *High Temp.* **53** 817–822
[3] Bellert D and Breckenridge W 2002 *Chem. Rev. (Washington, DC, U. S.)* **102** 1595–1622
[4] Le Roy R J Level code URL `http://leroy.uwaterloo.ca/programs/`
[5] Partridge H and Bauschlicher C W J 1994 *J. Phys. Chem.* **98** 2301–2306
[6] Hayes T, Bellert D, Buthelezi T and Brucat P J 1998 *Chem. Phys. Lett.* **287** 22–28
[7] Asher R L, Bellert D, Buthelezi T and Brucat P J 1994 *Chem. Phys. Lett.* **227** 277–282
[8] Sugar J and Corliss C 1985 *J. Phys. Chem. Ref. Data* **14** 1–664
[9] Gurvich L V, Veyts I V and Alcock C B 1989 *Thermodynamic Properties of Individual Substances* vol 1 (Hemisphere Publishing Corp.)
[10] Witte T M and Houk R S 2012 *Spectrochim. Acta, Part B* **69** 25–31