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

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

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

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

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 Schrödinger equation. As the result this code provides the energies of vibrational levels and the coefficients of polynomial for calculating the rovibronic energy levels

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

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-Brekenridge 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

\[
V_J(r) = V_0(r) + \left(\frac{\hbar}{8\pi^2\mu c}\right)J(J + 1)\frac{1}{r^2}.
\]
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

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

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 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 $Q_{\text{vib-rot}}$ for fifteen $\Omega$-states that correlate with spin-orbit components of the VAr$^+$ ground LS-term $^5\Sigma(3d^4)$ and for twelve $\Omega$-states that correlate with spin-orbit components of the CoAr$^+$ ground LS-term $^3\Sigma(3d^6)$. Potential curves of the $\Omega$-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 \(\Lambda S\)-states from [5] and experimental data on the dissociation energy \(D_0\) and the values of \(R_e\) for the ground \(\Omega\)-state: VAr\(^+\), \(\Omega = 0\), \(^5\Sigma_0^+\) [3, 6]; CoAr\(^+\), \(\Omega = 3\), \(^3D_3\) [3, 7]. The \(\Lambda S\)-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 \(T = 10000\) K the calculated \(Q_{\text{vib-rot}}\) 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 \(Q_{\text{vib-rot}}\) for the experimentally observed excited states \(^5\text{P}_1\) (3d\(^4\)4s) of VAr\(^+\) [3, 6]; \(^3\text{F}_4\) (3d\(^7\)4s) and \(^3\text{P}_2\) (3d\(^7\)4s) of CoAr\(^+\) [3, 7]. The rounded \(Q_{\text{vib-rot}}\) 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 \(Q_{\text{int}}\) for VAr\(^+\) and CoAr\(^+\). In the equation

\[
Q_{\text{int}} = \sum_{ik} g_{ik} Q_{\text{vib-rot}}^{ik} e^{-(E_{ik}-E_{0i})/k_B T},
\]

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
MAr$^+$, one can obtain

$$Q_{\text{int}} = \sum_i e^{(-E_i-E_0)/k_BT} \sum_k g_{ik} Q_{\text{vib-rot}}^{ik} e^{(D_0^{ik}-D_0)/k_BT}. \quad (7)$$

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

| $T$ K | $C_p^o(T)$ J K$^{-1}$ mol$^{-1}$ | $\Phi^o(T)$ | $S^o(T)$ K mol$^{-1}$ | $H^o(T) - H^o(0)$ kJ mol$^{-1}$ | $\lg K^o(T)$ | $\Delta_f H^o(0)$ kJ mol$^{-1}$ | $M$ = 90.8889 | $S_{\text{model}} = 17.682$ J K$^{-1}$ mol$^{-1}$ |
|-------|-----------------|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 298.150 | 50.503 | 225.307 | 263.468 | 11.378 | 2.8325 | 298.150 | 1128.800 | 17.682 |
| 300.000 | 50.634 | 225.541 | 263.781 | 11.471 | 2.7910 | 300.000 | 1135.958 | 17.682 |
| 400.000 | 53.332 | 237.071 | 278.884 | 16.728 | 1.1373 | 400.000 | 1143.114 | 17.682 |
| 500.000 | 51.757 | 246.651 | 290.659 | 22.002 | 0.1711 | 500.000 | 1150.270 | 17.682 |
| 600.000 | 48.690 | 254.782 | 299.837 | 27.031 | -0.4574 | 600.000 | 1157.426 | 17.682 |
| 700.000 | 45.145 | 261.761 | 307.079 | 31.724 | -0.8992 | 700.000 | 1164.582 | 17.682 |
| 800.000 | 41.604 | 267.803 | 312.874 | 36.060 | -1.2288 | 800.000 | 1171.738 | 17.682 |
| 900.000 | 38.346 | 273.079 | 317.583 | 40.055 | -1.4868 | 900.000 | 1178.894 | 17.682 |
| 1000.000 | 35.655 | 277.726 | 321.474 | 43.745 | -1.6968 | 1000.000 | 1186.050 | 17.682 |
| 1500.000 | 31.774 | 294.695 | 334.730 | 60.048 | -2.3825 | 1500.000 | 1192.106 | 17.682 |
| 2000.000 | 27.340 | 305.739 | 342.744 | 74.010 | -2.7976 | 2000.000 | 1198.162 | 17.682 |
| 2500.000 | 26.679 | 313.762 | 348.741 | 87.430 | -3.0968 | 2500.000 | 1204.218 | 17.682 |
| 3000.000 | 27.301 | 320.014 | 353.645 | 100.895 | -3.3313 | 3000.000 | 1210.274 | 17.682 |
| 4000.000 | 29.515 | 329.467 | 361.792 | 129.271 | -3.6874 | 4000.000 | 1216.330 | 17.682 |
| 5000.000 | 31.554 | 336.635 | 368.608 | 259.852 | -3.9544 | 5000.000 | 1222.386 | 17.682 |
| 6000.000 | 32.899 | 342.467 | 374.941 | 192.143 | -4.1682 | 6000.000 | 1228.442 | 17.682 |
| 7000.000 | 33.444 | 347.418 | 379.614 | 225.382 | -4.3462 | 7000.000 | 1234.498 | 17.682 |
| 8000.000 | 33.207 | 351.727 | 384.073 | 258.770 | -4.4987 | 8000.000 | 1240.554 | 17.682 |
| 9000.000 | 32.524 | 355.539 | 387.936 | 291.557 | -4.6323 | 9000.000 | 1246.610 | 17.682 |
| 10000.000 | 30.670 | 358.953 | 391.257 | 323.068 | -4.7516 | 10000.000 | 1252.666 | 17.682 |

Table 1. Thermodynamic functions for the vanadium argide positive ion.
Table 2. Thermodynamic functions for the cobalt argide positive ion.

| $T$ (K) | $C_p^o(T)$, J K$^{-1}$ mol$^{-1}$ | $\Phi^o(T)$, kJ mol$^{-1}$ | $S^o(T)$, J K$^{-1}$ mol$^{-1}$ | $H^o(T) - H^o(0)$, kJ mol$^{-1}$ | $\lg K^o(T)$ | $T$ (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                           | 276.363                   | 320.706                     | 48.477                          | -1.3702        | 1100.000|
| 1200.000| 40.684                           | 280.465                   | 324.330                     | 52.640                          | -1.5967        | 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|

\[ M = 98.895 \]

\[ \Delta_f H^o(0) = 1079.634 \text{ kJ mol}^{-1} \]

\[ \Delta_f H^o(298.15) = 1086.422 \text{ kJ mol}^{-1} \]

\[ S^o_{\text{mol}} = 17.526 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ \Phi^o(T) = 266.324211719 + 12.444517344 \ln(x) + 0.00294694886 x^{-2} - 0.57372212185 x^{-3} + 567.239024059 x - 1936.2937279628 x^2 + 2844.79727082856 x^3 \]

\( (x = T \times 10^{-4}; 298.15 < T < 1500 \text{ K}) \)

\[ \Phi^o(T) = 362.736632729 + 25.698789141 \ln(x) + 0.1329649529 x^{-2} - 4.3869317212 x^{-1} - 3.903295927355 x + 3.7869495837 x^2 - 0.983104635848 x^3 \]

\( (x = T \times 10^{-4}; 1500 < T < 10000 \text{ K}) \)

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$^n$4s configuration; c) the terms of other configurations M$^+$. 

These parts were calculated using the equation

$$Q_{\text{int}} = \sum_i g_i e^{-(E_i - E_0)/k_B T} Q^{\text{av}}_{\text{vib-rot}} e^{(D^{\text{av}}_0 - D_0)/k_B T},$$

(8)

where $Q^{\text{av}}_{\text{vib-rot}}$ and $D^0_{\text{av}}$ are approximate average values of $Q^{ik}_{\text{vib-rot}}$ and $D^{ik}_0$. For the part 2 we have estimated the values of $Q^{\text{av}}_{\text{vib-rot}}$ and $D^0_{\text{av}}$ using the values $Q^{ik}_{\text{vib-rot}}$ and $D^{ik}_0$ from the part 1. For the part 3 we have done the same but using the values $Q^{ik}_{\text{vib-rot}}$ and $D^{ik}_0$ for $5P_1(3d^74s), 3_2(3d^74s)$ states of CoAr$^+$ (see above). For the part 4 no values of $Q^{ik}_{\text{vib-rot}}$ and $D^{ik}_0$ are available, therefore we have accepted the values of $Q^{\text{av}}_{\text{vib-rot}}$ and $D^0_{\text{av}}$ as in the part 3. Note, that the part 4 correlates with high terms of M$^+$ and it constitutes less than 1.1% of $Q_{\text{int}}$ 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 VAr$^+/V^+$ at 6000 K would be of 68 ppm, and that of CoAr$^+/Co^+$ 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.

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