# Thermodynamics of the Electron Revisited and Generalized

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S *Supporting Information*

ABSTRACT: The accurate evaluation of redox potentials in various media and the ability of electron transfer in some biological or chemical reactions are subject to the determination of the accurate gas phase thermodynamic data of the electron. These data are also useful to describe with a high accuracy the movement of the electron in a stellar core. However, these data were not available at all temperatures, and the available data were not sufficiently accurate. I addressed this matter using a robust and reliable self-consistent iterative procedure which determines the entropy of a gas phase free electron and, thereafter, allows the calculation of its heat capacity, enthalpy, and free energy. Extremely accurate analytic expressions of the aforementioned thermodynamic parameters were provided at all temperatures. The thermodynamic parameters of the gas phase electron are now known at all temperatures (integer or noninteger) in the standard atmosphere with a high accuracy. Analytic expressions proposed for the thermodynamic parameters are highly advisable where iteratively computed data are unavailable. Note that at room temperature (T = 298.15 K), the values recommended for the thermodynamic parameters of the gas phase electron are S = 22.6432 J mol^{-1} K^{-1}, C_P = 17.1062 J mol^{-1} K^{-1}, ΔH = 3.1351 kJ mol^{-1}, and ΔG = −3.6160 kJ mol^{-1}.
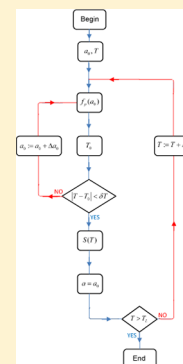
1. INTRODUCTION

The accurate evaluation of redox potentials in various media[1−3] and the ability of electron transfer in some biological or chemical reactions[4−8] are subject to the determination of the accurate gas phase thermodynamic data of the electron. Note that the electron movement also happens in a stellar core at temperatures reaching about 10^7 K and obeys different rules (classical or quantum) at different times during stellar evolution.[9]

However, the investigation of accurate thermodynamic parameters of the gas phase electron may be an open problem, since the entropy S of the quantum electron is not analytically soluble at all temperatures. In fact, although an analytic and asymptotic solution can be derived at extremely low temperatures ($T \leq 20$ K), there are no possible direct analytic solutions at higher temperatures. For $T > 315$ K, Mitchell[10] expanded the entropy to the power series of a limited number of terms to derive values of the entropy at 315, 406, and 492 K. He obtained a value of $S(298) = 22.72$ J mol^{-1}K^{-1} by means of a short extrapolation. Similarly, Gordon[11] only obtained Helmholtz free energies of the electron for 225 < T < 3275 K, although they were not presented explicitly. More recently, Bartmess[12] addressed the problem numerically using a self-consistent and more reliable procedure. However, a scrutiny of his results reveals some inconsistencies. The first inconsistency was noted at extremely low temperatures ($T \leq 20$ K). At these temperatures, his results reveal that $S(T) \neq C_P(T)$, whereas these two parameters should be as close as possible, as demonstrated in the Supporting Information (SI). Moreover, at low temperatures ($2 \leq T \leq 50$ K), the relative error on his enthalpy and Gibbs free energy ranges from 2 to 26%, see Table S2 in the SI. Such errors are unacceptable, since the relative error on the extremely accurate results should be less than 1%.

Furthermore, it is noteworthy that up to now, there are "no" data on the thermodynamics of the electron for $T > 1000$ K; though at these temperatures, the free electron is still degenerate as demonstrated further in this work. Note also the unavailability of data for noninteger temperatures. In regard to the less accurate available data on the thermodynamics of the electron and the lack of data at all temperatures, new computations of the thermodynamics of the electron, addressing the above points, would be of great interest to the scientific community. Thus, the main goal of this work is devoted to providing extremely accurate data for the thermodynamics of the electron, at all temperatures (in the broadest sense) in the standard atmosphere (P = 1 atm).

2. COMPUTATIONAL DETAILS

The thermodynamic parameters of the electron are investigated assuming a free electron gas treated as an ideal quantum gas and described in a grand canonical ensemble. For such a gas, the grand partition function is determined through the Fermi–Dirac statistics. Thereafter, the grand potential of the system is determined assuming the electrons to be enclosed in a cube and applying boundary conditions. More details are provided in the SI. Using this scheme leads to the following expression for the entropy of the electron quantum gas:

$$S(T) = \frac{5}{2} R \frac{f_{3/2}(a)}{f_{1/2}(a)} - R \ln a \tag{1}$$

where $f_{p \in \{(1/2),(3/2)\}}$ is defined as

$$f_p(a) = \frac{1}{p!} \int_0^{\infty} \frac{x^p}{1 + \frac{1}{a}e^x} \, dx, \quad a = e^{\mu/k_B T},$$

$$p \in \left\{ \frac{1}{2}, \frac{3}{2} \right\} \tag{2}$$

R, a, μ, k_B, and T are, respectively, the ideal gas constant, an undetermined parameter representing the whole degeneracy of the electron quantum gas, the chemical potential, the Boltzmann constant, and the temperature in Kelvin (K). Likewise, the temperature of the electron quantum gas can be derived as

$$T = \left[\frac{P^\circ h^3}{gk(2\pi m_e k_B)^{3/2} f_{3/2}(a)} \right]^{2/5} \tag{3}$$

where P°, g, and h are, respectively, the standard atmosphere, the electron degeneracy ($g = 2$), and the Planck constant. The other parameters in this equation have the same meaning as in the previous equations.

It is worth remarking that eq 1 cannot be solved analytically, since the parameter a is unknown. Thus, to address this matter I used a numerical approach similar to the one of Bartmess.[12] This approach is an iterative and self-consistent procedure based on the computed temperature as defined in eq 3. The convergence threshold of the computed temperatures is determined to be $\delta T = 10^{-6}$ K. Details were discussed in the next section. The flowchart of this procedure is presented in Figure 1.

The integration procedure to perform the computation of $f_p(a)$ was ensured using the Romberg integration method. In this scheme, the absolute error used was 10^{-8}, since higher precision does not change the computed temperature within its absolute error. Moreover, the upper limit of the integration in the expression of $f_p(a)$ was determined through the vanish point of the integrand. This vanish point is found to be 505 units for temperatures lower than 20 K and 80 units for higher temperatures.

The heat capacity was computed as $C_P(T) = T((\partial S)/(\partial T))_P$, and the differentiation was performed using the three-points differentiation method. The enthalpy was computed applying Simpson's rule with the formula $\Delta H(T) = \int_0^T C_P(u) \, du$. As for the Gibbs free energy, it was calculated as $\Delta G(T) = \Delta H(T) - T\Delta S(T)$. Throughout this work, "free energy" without any specification refers to the Gibbs free energy.

Analytic expressions for thermodynamic parameters of the electron were derived fitting the numerical obtained data to polynomial functions. Fits were performed using the Leven-berg–Marquardt method.[13,14]

3. RESULTS AND DISCUSSION

3.1. Computed Data. This work started by a scrutiny of data provided earlier by Bartmess, Table S1 (in SI).[12] Thus, absolute and relative errors on the entropy, heat capacity, enthalpy, and free energy of the electron at available temperatures were first calculated from those data and reported in Table S2 (see SI). All of these relative errors decrease as the temperature increases. The relative errors on S and C_P are very low and may be acceptable. Meanwhile, at very low temperatures ($2 \leq T \leq 50$ K), the relative error on the enthalpy and free energy range from 2 to 26%. Such errors are unacceptable, since the relative error on the extremely accurate
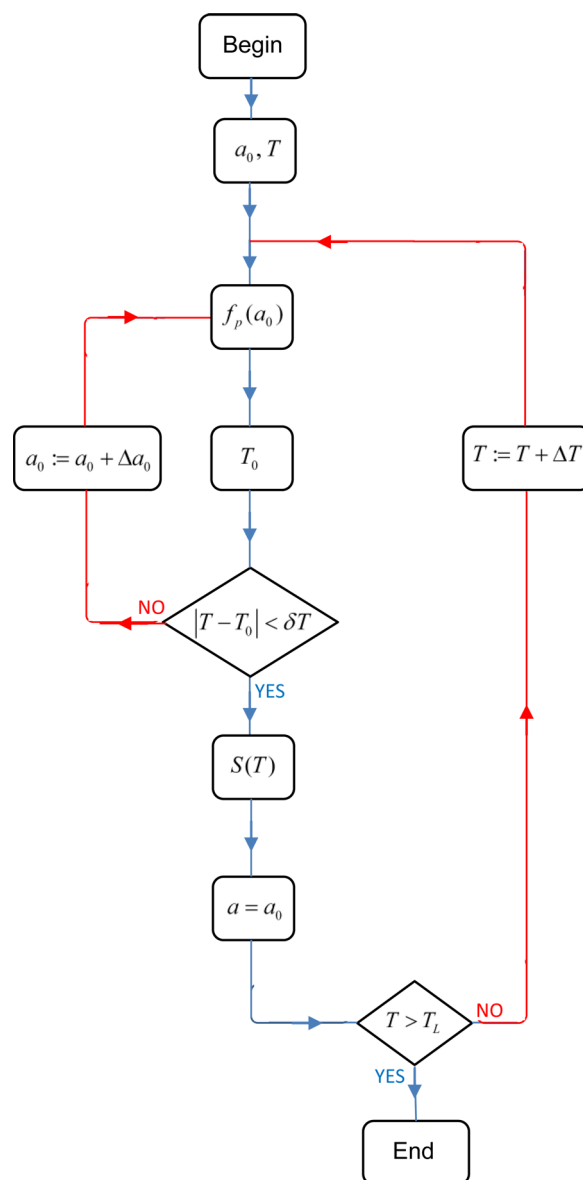
Figure 1. Flowchart of the procedure computing the entropy S of a gas phase electron at a given temperature T. a_0 is the trial value for the unknown parameter a. f_p is the function defined in eq 2. T_0 is the estimated temperature related to a_0 and computed using eq 3. T_L is the desired limit value of the temperature. δT is the convergence threshold of the estimated temperatures. In this simulation, $T_L = 10^4$ K and $\delta T = 10^{-6}$ K. Justification is provided further in this paper. $\Delta T = 1$ K is the temperature change step; Δa_0 is the change step for a_0 and depends strongly on the latter. In this algorithm, the inner loop is self-consistent.

results should be less than 1%. This may be the manifestation of extensive errors in the computation of S and C_P at extremely low temperatures ($T \leq 20$ K). As a matter of fact, for this range of temperatures, eq 1 can be simplified to

$$S(T) = C_P(T) \simeq \frac{\pi^2}{2} R \frac{T}{T_F} \tag{4}$$

with a maximum displacement of 5×10^{-3} J mol^{-1}, where T_F is the Fermi temperature (degeneracy temperature) of the electron quantum gas. This requirement is not fulfilled by the results pointed out by Bartmess.[12] Another inconsistency in his

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Table 1. Calculated and Fitted Data for the Entropy, Heat Capacity, Enthalpy, and Free Energy of the Gas Phase Electron[a]

T	S(cal.)	S(fit.)	C_P(cal.)	C_P(fit.)	ΔH(cal.)	ΔH(fit.)	ΔG(cal.)	ΔG(fit.)
0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	−0.0000	−0.0000
1.00	0.0855	0.0855	0.0855	0.0854	0.0000	0.0000	−0.0000	−0.0000
2.00	0.1709	0.1709	0.1709	0.1709	0.0002	0.0002	−0.0002	−0.0002
5.00	0.4273	0.4273	0.4274	0.4274	0.0011	0.0011	−0.0011	−0.0011
10.00	0.8549	0.8549	0.8553	0.8554	0.0043	0.0043	−0.0043	−0.0043
20.00	1.7111	1.7112	1.7149	1.7149	0.0171	0.0171	−0.0171	−0.0171
50.00	4.2979	4.2979	4.3337	4.3337	0.1077	0.1077	−0.1072	−0.1071
100.00	8.6009	8.6010	8.4391	8.4391	0.4300	0.4300	−0.4301	−0.4301
150.00	12.6679	12.6679	11.6930	11.6930	0.9370	0.9370	−0.9632	−0.9632
200.00	16.3826	16.3826	14.1239	14.1239	1.5855	1.5855	−1.6910	−1.6909
250.00	19.7347	19.7346	15.8881	15.8881	2.3383	2.3383	−2.5954	−2.5953
273.15	21.1702	21.1701	16.5240	16.5241	2.7145	2.7136	−3.0682	−3.0689
298.15	22.6432	22.6431	17.1062	17.1063	3.1351	3.1342	−3.6160	−3.6167
300.00	22.7491	22.7490	17.1454	17.1455	3.1659	3.1659	−3.6588	−3.6586
350.00	25.4629	25.4628	18.0371	18.0372	4.0467	4.0467	−4.8653	−4.8650
400.00	27.9153	27.9152	18.6732	18.6733	4.9654	4.9654	−6.2008	−6.2003
450.00	30.1427	30.1425	19.1329	19.1328	5.9111	5.9111	−7.6531	−7.6525
500.00	32.1769	32.1767	19.4703	19.4703	6.8766	6.8766	−9.2118	−9.2110
600.00	35.7696	35.7694	19.9136	19.9136	8.8478	8.8478	−12.6139	−12.6125
700.00	38.8607	38.8604	20.1769	20.1770	0.8534	10.8534	−16.3491	−16.3468
800.00	41.5666	41.5663	20.3427	20.3428	12.8800	12.8800	−20.3733	−20.3698
900.00	43.9694	43.9691	20.4523	20.4523	14.9201	14.9201	−24.6523	−24.6475
1000.00	46.1284	46.1281	20.5273	20.5278	16.9694	16.9694	−29.1590	−29.1590
2000.00	60.4503	60.4503	20.7395	20.7396	37.6429	37.6429	−83.258	−83.258
3000.00	68.8664	68.8660	20.7692	20.7692	58.4007	58.4006	−148.199	−148.199
4000.00	74.8428	74.8424	20.7779	20.7779	79.1749	79.1749	−220.196	−220.196
5000.00	79.4797	79.4796	20.7814	20.7814	99.9548	99.9548	−297.443	−297.443
6000.00	83.2687	83.2686	20.7832	20.7831	120.7372	120.7372	−378.875	−378.875
7000.00	86.4725	86.4723	20.7841	20.7840	141.5209	141.5208	−463.787	−463.787
8000.00	89.2479	89.2473	20.7847	20.7846	162.3053	162.3053	−551.678	−551.678
9000.00	91.6960	91.6945	20.7851	20.7850	183.0902	183.0902	−642.174	−642.174
10000.00	93.8860	93.8829	20.7853	20.7854	203.8754	203.8754	−734.984	−734.984

[a]The abbreviations cal. and fit. stand respectively for the calculated and fitted data. The calculated values were obtained using an iterative and self-consistent procedure addressing eq 1 where the parameter a is unknown. Those of the other thermodynamic parameters were obtained by differentiation or integration of data. The fitted data were obtained applying the Levenberg−Marquardt method[13,14] to the data previously obtained. The entropy and heat capacity are given in J mol^{-1} K^{-1}, while the enthalpy and free energy are given in KJ mol^{-1}

data (provided by e-mail) was noted on C_P for $T \geq 451$ K, Table S1. From this temperature, the heat capacity provided by Bartmess is not a strictly monotonous function of the temperature as would be expected, in regard to the definition of C_P. This is very glaring at higher temperatures and may be explained by the fact that at high temperatures, the heat capacity does not change much and its change becomes lower than the absolute error allowed by the precision used by Bartmess. All of these inconsistencies strongly indicate that the precision of the computation of the estimated temperature should be enhanced. Thus, the cutoff value of 4×10^{-4} K for δT, as used by Bartmess, may not be sufficient.

Regarding all of the aforementioned inconsistencies, I recomputed the thermochemistry data for the free electron at $T = 1$ K, reducing the cutoff value of the estimated temperature to 10^{-6} K. Thereafter, relative errors on the enthalpy and free energy were also recalculated with this new value of δT. Serendipitous results were obtained, 0.2% for both! Thus this new value of δT was retained for further computations at higher temperatures, since the calculated relative errors would decrease with an increasing of the temperature (See eqs 27 and 28 in the SI).

Once a reliable cutoff value for the estimated temperature is determined, it would be more appropriate to evaluate the temperature span in which the electron gas can be considered as degenerate. Beyond this span, the electron gas could be considered as classical and nondegenerate. For this aim, I calculated the Fermi temperature using eq 4 for $T = 1$ K. The result obtained is $T_F = 480$ K and $\varepsilon_F = 0.04$ eV. From these values, the electron density and the mean distance between electrons were calculated to be 3.6×10^{25} electrons/cm^3 and 3.02 nm, respectively. Usually, a quantity Q_1 is said to be negligible as compared to a quantity Q_2 if the former is less than 5% of the latter. Thereby, the free electron gas could be considered as a quantum gas for temperatures ranging from 0 to $T_L = 10^4$ K. Beyond this limit, it could be considered as a classical gas, and the Sackur−Tetrode equation (eq 5) could be used for the entropy instead of eq 1:

$$S_{cl}(T) = \frac{5}{2}R + R \log\left[\frac{(2\pi m_e k_B T)^{3/2} k_B T}{P^\circ h^3} g\right] \qquad (5)$$

The variables in this equation have the same meanings as described previously. This new equation simplifies computa-

tions in this temperature range, since the above-mentioned iterative procedure would no more be applied.

Having in hand the cutoff value of the estimated temperature and the temperature span in which the electron gas can be considered as degenerate, I computed the entropy, heat capacity, and free energy of the degenerate electron gas for all integer temperatures ranging from 0 to 10^4 K, Table 1 and Figure 2. Complete data were reported in Table S3 (see SI). At
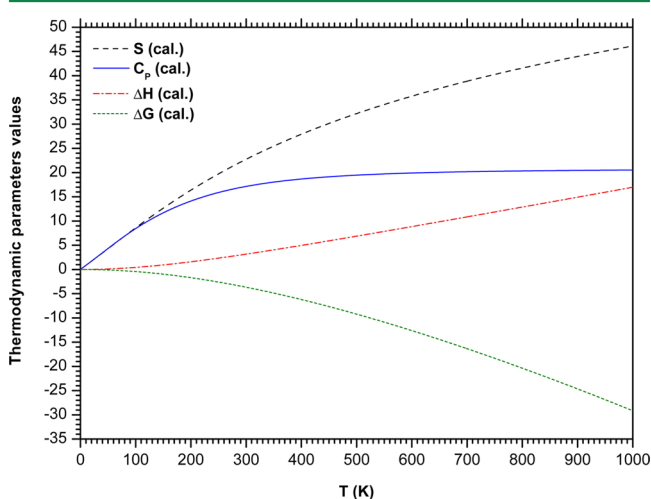
Figure 2. Plot of the calculated entropy (S(cal.)), heat capacity (C_P(cal.)), enthalpy (ΔH(cal.)), and free energy (ΔG(cal.)) of the gas phase electron, for temperatures ranging from 0 to 1000 K in the standard atmosphere. S(cal.) and C_P(cal.) are given in J mol^{-1}K^{-1}, while ΔH(cal.) and ΔG(cal.) are in kJ mol^{-1}).

very low temperatures ($T \leq 20$ K), $S(T) = C_P(T)$ with an acceptable maximum displacement which is lower than 4×10^{-3} J mol^{-1}. Moreover, the strict monotony of all the computed thermodynamic parameters can now be appreciated. Furthermore, the absolute and relative errors on those parameters were also computed and reported in Table S4 (see SI). Relative errors reported there are extremely low (<1%) at all temperatures. Thus, my computed parameters are extremely accurate and may be highly recommended for future works. Elsewhere, the entropy and heat capacity were also computed at some temperatures at the standard pressure (10^5 Pa) and are reported in the Table S9 (see SI). The values obtained show that pressure effects are very significant and should retain our attention in further investigations. In addition, the Bartmess results[12] slightly (0.6%) overestimate the exact values of the entropy and significantly underestimate (15%) the heat capacity at very low temperatures ($T \leq 10$ K). Thus, his results would lead to an underestimation of enthalpy and free energy at all temperatures.

3.2. Data Fitting. In order to provide analytic expressions of S, C_P, ΔH, and ΔG for the free electron, I fitted the data obtained numerically to polynomial functions. For the sake of extremely accurate fit parameters, the temperature range of 0 to 10^4 K was subdivided into the smallest intervals. Details on the polynomial expansion of fitted data from iteratively computed ones, for each thermodynamic parameter, are explicitly reported in Tables S5–S8 (see SI). The correlations of all fit functions related to each thermodynamic parameter were found to be equal to 1, while the standard deviations (STD) were lower than 10^{-6} units.

3.2.1. Fit for S. Fits for S were performed splitting the temperature range into 10 subintervals, and analytic expressions for S were proposed, depending on the temperature range. Thus,

● For 200 K $\leq T \leq$ 800 K,

$$S(T) = \left(\sum_{k=l_{min}}^{l_{max}} s_k^{(n)} T^k \right) \times \log(T) \tag{6}$$

● For 0 K $\leq T \leq$ 200 K and 800 K $\leq T \leq T_L$,

$$S(T) = \sum_{k=l_{min}}^{l_{max}} s_k^{(n)} T^k \tag{7}$$

● For $T > T_L$,

$$S(T) = S_{cl}(T) \text{ (Sackur−Tetrode equation)} \tag{8}$$

In fact, from 0 to 10^4 K, the difference $S(T) - S_{cl}(T)$ decreases and converges toward zero at $T = T_L$. This is an indication of the convergence of Boltzmann and Fermi−Dirac statistics at high temperatures and could add a lot of credibility to the algorithm implemented to compute the entropy. Thus, with an extremely high accuracy, one can state that $S(T) = S_{cl}(T)$ for $T > 10\,000K = T_L$. Therefore, for this temperature range, the free electron gas may be described properly and merely as a classical gas.

In eqs 6 and 7, $s_k^{(n)}$ represents the k-order parameter of the nth fit function for the entropy S. Similar denominations were assumed for $c_k^{(n)}$, $h_k^{(n)}$, and $g_k^{(n)}$ used below.

3.2.2. Fit for C_P. Fits for C_P were performed splitting the temperature range into 10 subintervals, and analytic expressions for C_P were proposed depending on the temperature range. Thus,

● For 0 K $\leq T \leq T_L$,

$$C_P(T) = \sum_{k=l_{min}}^{l_{max}} c_k^{(n)} T^k \tag{9}$$

● For $T > T_L$,

$$C_P(T) = C_P(T_L) = 20.7853 \, \text{J mol}^{-1} \, \text{K}^{-1} \tag{10}$$

In fact, C_P increases as the temperature increases and converges at $T = T_L$, Figure 2 or Table S3. Thus, it would be reasonable to assume the value of $C_P(T_L)$ for C_P at higher temperatures. In addition, at $T = T_L$, the relative error between the computed value and the expected one $((5/2)R)$ is about 0.004%, which is extremely low and can be assumed to be nil. Thus, at $T = T_L$ the computed value of C_P and the expected one are in excellent agreement. This reinforces and confirms the statement made earlier and suggests the treatment of the free electron gas as a classical gas for $T > T_L$.

3.2.3. Fit for ΔH. Fits for ΔH were performed splitting the temperature range into seven subintervals, and analytic expressions for ΔH were proposed depending on the temperature range. Thus,

● For 0 K $\leq T \leq T_L$,

$$\Delta H = \sum_{k=l_{min}}^{l_{max}} h_k^{(n)} T^k \tag{11}$$

● For $T > T_L$,

$$\Delta H(T) = \Delta H(T_L) + C_P(T)(T - T_L) \tag{12a}$$

$$= -3.9776 + 0.0207853 \times T \tag{12b}$$

Here, ΔH is given in kJ mol^{-1}, and I used the fact that C_P is constant and equals $C_P(T_L)$ in this temperature range.

3.2.4. Fit for ΔG. Fits for ΔG were performed splitting the temperature range into five subintervals, and analytic expressions for ΔG were proposed depending on the temperature range. Thus,

- For $0\ \mathrm{K} \leq T \leq 1000\ \mathrm{K}$,

$$\Delta G(T) = \left(\sum_{k=l_{\min}}^{l_{\max}} g_k^{(1)} T^k \right) \times \log(T + 1) + \sum_{k=1}^{3} g_{k+l_{\max}}^{(1)} T^k \tag{13}$$

- For $1000\ \mathrm{K} \leq T \leq T_L$,

$$\Delta G(T) = \sum_{k=l_{\min}}^{l_{\max}} g_k^{(n)} T^k \tag{14}$$

- For $T > T_L$,

$$\Delta G(T) = \Delta H(T_L) + C_P(T)(T - T_L) - T S_{cl}(T) \tag{15a}$$

$$= -3.9776 + (0.0207853 - S_{cl}(T)) T \tag{15b}$$

Here, ΔG is given in kJ mol^{-1}, taking into account results related to $\Delta H(T)$ and S in this temperature range. In eq15b, S_{cl} must be given in kJ mol^{-1}.

In the light of the extremely low STD and the 100% correlation noted in the fitted data obtained, one can state that the fitted data reproduce excellently the iteratively computed data. Elsewhere, for some noninteger temperatures, thermodynamic data obtained using the fitted functions were compared to those obtained by linear interpolation from integer temperatures. The results are in perfect agreement. Thus, the thermodynamic data at noninteger temperatures could be derived using either the explicit scheme (fitted functions) or the implicit one (linear interpolation from the table entries) depending on the need. In addition, the reliability of fitted data for noninteger temperatures may be ensured reporting the entropy and heat capacity with three significant figures, while the enthalpy and free energy are reported with two significant figures.

4. CONCLUSION

In this work, the thermodynamic parameters of the gas phase free electron were revised and generalized at all temperatures in the standard atmosphere. The free electron gas was treated as an ideal quantum gas and described in a grand canonical ensemble. The entropy of the free electron was computed using a self-consistent iterative procedure for integer temperatures ranging from 0 to 10 000 K. For higher temperatures, the Sackur–Tetrode expression was used instead. Thereafter, the heat capacity, enthalpy, and free energy of the free electron were derived at any temperature. The results obtained were fitted, and analytic expressions for all thermodynamic parameters of the free electron were proposed.

The thermodynamic parameters of the electron are now known at all temperatures (integer or noninteger) in the standard atmosphere with a high accuracy. Analytic expressions proposed for the thermodynamic parameters are highly advisable where iteratively computed data are unavailable. The extension of this work for other pressures could also be recommended in future investigations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General information related to the thermodynamics of the free electron gas, fit functions, computed entropy, heat capacity, enthalpy, and free energy of the free electron gas for $0\ \mathrm{K} \leq T \leq 10^4\ \mathrm{K}$ are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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