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# Revision of the Thermodynamics of the Proton in Gas Phase

Jean Jules Fifen,*,[†] Zoubeida Dhaouadi,[‡] and Mama Nsangou[§]

[†]Department of Physics, Faculty of Science, The University of Ngaoundere, P.O. Box 454, Ngaoundere, Cameroon

[‡]Laboratoire de Spectroscopie Atomique et Moléculaire, Faculté des Sciences de Tunis, Université de Tunis El Manar, Campus Universitaire 1060, Tunis, Tunisia

[§]University of Maroua, P.O. Box, 46, Maroua, Cameroon

Ⓢ *Supporting Information*

**ABSTRACT:** Proton transfer is ubiquitous in various physical/chemical processes, and the accurate determination of the thermodynamic parameters of the proton in the gas phase is useful for understanding and describing such reactions. However, the thermodynamic parameters of such a proton are usually determined by assuming the proton as a classical particle whatever the temperature. The reason for such an assumption is that the entropy of the quantum proton is not always soluble analytically at all temperatures. Thereby, we addressed this matter using a robust and reliable self-consistent iterative procedure based on the Fermi−Dirac formalism. As a result, the free proton gas can be assumed to be classical for temperatures higher than 200 K. However, it is worth mentioning that quantum effects on the gas phase proton motion are really significant at low temperatures ($T \leq 120$ K). Although the proton behaves as a classical particle at high temperatures, we strongly recommend the use of quantum results at all temperatures, for the integrated heat capacity and the Gibbs free energy change. Therefore, on the basis of the thermochemical convention that ignores the proton spin, we recommend the following revised values for the integrated heat capacity and the Gibbs free energy change of the proton in gas phase and, at the standard pressure (1 bar): $\Delta H_{0 \rightarrow T} = 6.1398$ kJ mol$^{-1}$ and $\Delta G_{0 \rightarrow T} = -26.3424$ kJ mol$^{-1}$. Finally, it is important noting that the little change of the pressure from 1 bar to 1 atm affects notably the entropy and the Gibbs free energy change of the proton.
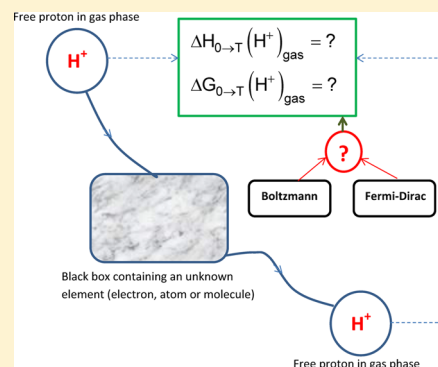
## 1. INTRODUCTION

The evaluation of several thermodynamic quantities of chemical compounds or physical/chemical processes depends strongly on the integrated heat capacity, the Gibbs free energy or more generally, on the thermodynamic parameters of the proton (TPP) in gas phase. Many authors[1−23] used these parameters for the accurate evaluations of solvation energies of the proton in some media, p$K_a$'s, absolute potential of the standard hydrogen electrode, proton affinities, and proton dissociation free energies. Thus, to ensure a good accuracy on those quantities, the accurate values of the thermodynamic parameters of the gas phase proton are highly recommended.

The proton is a Fermion, and therefore Fermi−Dirac statistical mechanics is the suitable formalism to be used.[24−26] Recently, Marenich et al.[23] emphasized the necessity to use the Fermi−Dirac formalism on the evaluation of the TPP, to expect accurate prediction on the absolute potential of the standard hydrogen electrode. However, using such a formalism for the proton leads to an entropy (of the quantum proton) that is not soluble analytically at all temperatures. By this way, the other thermodynamic parameters (heat capacity, enthalpy, free energy, ...) cannot be accessible directly. Thus, for the sake of simplicity, the proton is usually treated as a classical particle and described by the Boltzmann statistic at all temperatures. Of course, doing so could be less accurate, especially at low

temperatures where quantum effects are expected to be noticeable. So, what is the amount of error done through such an approximation? Is this approximation acceptable at all temperatures? If not, when does the proton cease to be treated as a classical particle?

Up to now, the only reliable approach involving the quantum nature of the proton has been proposed in 1994 by Bartmess,[27,28] who addressed the problem numerically using a self-consistent procedure. The work of Bartmess[27,28] numerically improved on the original 1928 calculations done by hand by Mitchell[29] who derived the explicit expression of the entropy of the electron, on the basis of earlier work of Sommerfeld.[25] However, a scrutiny of Bartmess'[27,28] results reveals some inconsistencies. The first one is noted at extremely low temperatures. In this temperature range, the entropy and the heat capacity of the proton should be the same within a high precision and likewise for the integrated heat capacity and the Gibbs free energy change. Bartmess' results do not show such features. The second incompatibility concerns the oscillations of the proposed values for the heat capacity at $T \geq 150$ K. This could be an artifact of computations, because the heat capacity

of the free proton gas should be an increasing function of the temperature, as we showed further in this manuscript. The third one is related to the different values obtained for the heat capacity at some temperatures, in the Boltzmann formalism. In such a formalism, the heat capacity should be the same at all temperatures (see subsection 2.2, for details). The fourth disagreement is that the author obtained the same values for the integrated heat capacities in Boltzmann and Fermi−Dirac formalisms at $T \leq 350$ K. This may be an error, because both quantities are already significantly different at lower temperatures. Only the increment of these quantities should be the same at very high temperatures (classical limit), because both formalisms are equivalent at this range of temperatures. Another fickleness is based on considerable errors noted on the heat capacities reported, especially at very low temperatures. The relative errors are up to 50% at 1 K. The discussion on this statement is provided later in the paper. The explanations of these discrepancies may be ascribed to numerical methods used to perform integrations, the cutoff value, or step size chosen for the computed temperatures, and finally to the old 1986 CODATA values used for physical constants.

It is also important to note that up to now, no data of TPP were available either for noninteger temperatures or for pressures different from 1 bar. Usually, the TPP obtained from 1 calculations were assumed at 1 atm, due to the lack of these data at this pressure. This assumption seems to be acceptable, because both pressures are very close. What is the truth behind this?

In regard to all that precedes, we think that it is timely to revise the thermodynamics of the proton in the gas phase. Thus, providing accurate data at all temperatures (integer and noninteger) in various pressures would be prominent for future works involving the thermodynamic parameters of the proton in the gas phase or in a solvent.

## 2. FORMALISM OF A FREE QUANTUM GAS

Throughout this work, we mean by proton, the free proton. The thermodynamics of the proton is investigated by assuming a free proton gas treated as an ideal quantum gas described in a grand canonical ensemble. All the thermodynamic parameters of the proton (TPP) were derived from the entropy of the quantum proton gas. The explicit expression of this entropy was first derived by Mitchell,[29] on the basis of the work of Sommerfeld.[25] For such a gas, the grand partition function follows the Fermi−Dirac statistic and it is defined as

$$Z_{\mathrm{G}} = \prod_p \left[1 + e^{-\beta(\varepsilon_p - \mu)}\right] \tag{1}$$

where $\varepsilon_p$ and $\mu$ are respectively the $p$th accessible energy level and the chemical potential of the system. $\beta = 1/k_{\mathrm{B}}$ with $k_{\mathrm{B}}$ the Boltzmann constant. Likewise, the grand potential of the aforementioned system is defined as

$$\Phi = -\frac{1}{\beta} \log Z_{\mathrm{G}} = -\frac{1}{\beta} \sum_p \log[1 + e^{-\beta(\varepsilon_p - \mu)}] \tag{2}$$

Assuming the particles to be enclosed in a cube of fixed edge length and applying periodic boundary conditions lead to (in the limit of large volume $V$)

$$\Phi = -\frac{2}{3}\frac{gVm^{3/2}}{\sqrt{2}\,\pi^2\hbar^3} \int_0^\infty \frac{\varepsilon^{3/2}}{1 + e^{\beta(\varepsilon-\mu)}}\, d\varepsilon \tag{3}$$

$$= -\frac{gVk_{\mathrm{B}}T}{\lambda^3} f_{3/2}(a) \tag{4}$$

where $g$ stands for the proton spin degeneracy ($g = 2$) and $m$ is for the rest mass of the proton. $T$ is the temperature considered and $\lambda = h/(2\pi mk_{\mathrm{B}}T)^{1/2}$ is the de Broglie wavelength. $\hbar$ is the Planck's constant ($h$) over $2\pi$. The function $f_p$ is defined as

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

$$a = e^{\mu/k_{\mathrm{B}}T}, \; p \in \left\{\frac{1}{2}; \frac{3}{2}\right\} \tag{5}$$

$a$ represents the whole degeneracy of the quantum gas.

Elsewhere, the average particles number is given by

$$N = \left(\frac{\partial \Phi}{\partial \mu}\right)_\beta = \sum_p n(\varepsilon_p) \tag{6}$$

where $n(\varepsilon_p)$ is the number of particles at the energy level $\varepsilon_p$. Using the same procedure (converting $\sum$ to $\int$) as for $\Phi$ leads to

$$N = \frac{gVm^{3/2}}{\sqrt{2}\,\pi^2\hbar^3} \int_0^\infty \frac{\varepsilon^{1/2}}{1 + e^{\beta(\varepsilon-\mu)}}\, d\varepsilon = \frac{gV}{\lambda^3} f_{1/2}(a) \tag{7}$$

Thus, using eqs 4 and 7, the grand potential can also be expressed for a mole of particles as

$$\Phi = -RT\frac{f_{3/2}(a)}{f_{1/2}(a)} \tag{8}$$

As for the internal energy of the proton gas,

$$U = \sum_p \varepsilon_p n(\varepsilon_p) = -\frac{3}{2}\Phi \tag{9}$$

After all, using the Gibbs−Duhem relation leads to the expression of the entropy

$$S = \frac{U + PV}{T} - \frac{\mu N}{T} \tag{10}$$

$$= \frac{5}{2}R\frac{f_{3/2}(a)}{f_{1/2}(a)} - R \ln a \tag{11}$$

$N$, $\Phi$, $U$, and $S$ aforementioned depend on the unknown whole degeneracy $a$ of the system. Note that the temperature can be derived from eq 4 conjointly with the definition $\Phi = -PV$ (for a homogeneous system):

$$T = \left[\frac{P°h^3}{gk_{\mathrm{B}}(2\pi mk_{\mathrm{B}})^{3/2}f_{3/2}(a)}\right]^{2/5} \tag{12}$$

where $P°$ is the gas pressure. The other parameters in this equation have the same meanings as in the previous equations. Note that the values for all constants used in this work are the "2010 CODATA recommended values".[30,31] So far, these values are the latest available.

It is worth remarking that eq 11 cannot be solved analytically at all temperatures, due to the presence of Fermi integrals $f_p$, in which the parameter $a$ is unknown. In regard to the interest of the Fermi integrals, their analytic approximations attracted several researchers.[32−39] In this work, rather than using proposed approximation methods to evaluate Fermi integrals and derive the entropy, we used a numerical approach similar to the one proposed by Bartmess.[27,28] This approach is an iterative and self-consistent procedure based on the computed temperature as defined in eq 12. Analytic results for special cases (completely degenerate and nondegenerate gas) have been discussed below.

Note that throughout this work, the TPP investigated are the internal energy ($U(T)$), the entropy ($S(T)$), the heat capacity ($C_p(T)$), the integrated heat capacity ($\Delta H_{0\to T}$), and the Gibbs free energy change ($\Delta G_{0\to T}$) at a given temperature $T$.

**2.1. Case of the Completely Degenerate gas ($a \to \infty$).** The completely degenerate gas is observed for $a \to \infty$, which corresponds to $T \to 0$. In this case, the famous Sommerfeld expansion[25] for the Fermi integrals is known to be very accurate.[37−39] On the basis of Sommerfeld's ideas,[25] we provided the following explicit expressions of the TPP at very low temperatures. Planting

$$\Lambda(T) = \left(\frac{6\pi^2}{g}\right)^{2/3} \frac{\hbar}{2m} \rho(T)^{2/3} \tag{13}$$

with $\rho(T) = N/V$ the proton density of the considered gas at a temperature $T$, the Fermi energy can be defined as $\varepsilon_F = \Lambda(0)$.

Equations 3 and 7 can be rewritten in terms of $\Lambda$:

$$\Phi(T) = -N\Lambda(T) \int_0^\infty \frac{\varepsilon^{3/2}}{1 + e^{\beta(\varepsilon-\mu)}}\, d\varepsilon \tag{14}$$

$$1 = \frac{3}{2}\Lambda(T)^{-3/2} \int_0^\infty \frac{\varepsilon^{1/2}}{1 + e^{\beta(\varepsilon-\mu)}}\, d\varepsilon \tag{15}$$

Planting also $I_p = \int_0^\infty u_p(\varepsilon)\, n(\varepsilon)\, d\varepsilon$, with $n(\varepsilon) = 1/(1 + e^{\beta(\varepsilon-\mu)})$ and $u_p(\varepsilon) = \varepsilon^p$, $p \in \{^1/_2;\ ^3/_2\}$, we can write

$$I_p = \int_0^\mu u_p(\varepsilon)\, d\varepsilon + \int_0^\infty u_p(\varepsilon)[n(\varepsilon) - \Theta(\mu - \varepsilon)]\, d\varepsilon \tag{16}$$

$$= \int_0^\mu u_p(\varepsilon)\, d\varepsilon + \int_{-\infty}^\infty u_p(\varepsilon)[n(\varepsilon) - \Theta(\mu - \varepsilon)]\, d\varepsilon \tag{17}$$

with $\Theta$ being the step function. Remark that $[n(\varepsilon) - \Theta(\mu - \varepsilon)]$ differs from zero only in the neighborhood of $\varepsilon = \mu$. Thus, expanding $u_p(\varepsilon)$ around the value $\mu$ in a Taylor series and introducing a new integration variable, $x = (\varepsilon - \mu)/k_B T$, leads to

$$I_p = \int_0^\mu u_p(\varepsilon)\, d\varepsilon + 2\sum_{l=0}^\infty (k_B T)^{2l+2} \cdot \frac{u_p^{(2l+1)}(\varepsilon)}{(2l+1)!} \int_0^\infty \frac{x^{2l+1}}{1 + e^x}\, dx \tag{18}$$

$$= \int_0^\mu u_p(\varepsilon)\, d\varepsilon + 2\sum_{l=0}^\infty \sum_{k=1}^\infty \frac{(-1)^{k-1}}{k^{2l+2}} u_p^{(2l+1)}(\varepsilon)(k_B T)^{2l+2} \tag{19}$$

Thus, $f_{1/2}$ and $f_{3/2}$ can be expressed as

$$f_{3/2}(a) = S_{3/2}\left[\frac{2}{5} + \frac{\pi^2}{4}\left(\frac{k_B T}{\mu}\right)^2 + \frac{7\pi^4}{480}\left(\frac{k_B T}{\mu}\right)^4\right]$$
$$- 3S_{3/2}\left[\sum_{l=2}^\infty \sum_{k=1}^\infty \frac{(-1)^{k-1}}{k^{2l+2}} \frac{(4l-3)!}{2^{4l-2}(2l-2)!}\left(\frac{k_B T}{\mu}\right)^{2l+2}\right] \tag{20}$$

$$f_{1/2}(a) = S_{1/2}\left[\frac{2}{3} + \sum_{l=0}^\infty \sum_{k=1}^\infty \frac{(-1)^{k-1}}{k^{2l+2}} \frac{(4l)!}{2^{4l}(2l)!}\left(\frac{k_B T}{\mu}\right)^{2l+2}\right] \tag{21}$$

with $S_p = (1/(p)!)(\mu/k_B T)^{p+1}$.

Reducing $f_p$ to its first three terms and introducing the Fermi temperature $T_F = \varepsilon_F/k_B$, we have

$$U(T) = \frac{3}{5}N\varepsilon_F\left[1 + \frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2 - \frac{\pi^4}{36}\left(\frac{T}{T_F}\right)^4 + O(T^6)\right] \tag{22}$$

$$C_p(T) = \frac{\partial U}{\partial T} = \frac{\pi^2}{2}R\left[\left(\frac{T}{T_F}\right) - \frac{3\pi^2}{10}\left(\frac{T}{T_F}\right)^3 + O(T^5)\right] \tag{23}$$

$$S(T) = \int_0^T \frac{C_p(u)}{u}\, du \tag{24}$$

$$= \frac{\pi^2}{2}R\left[\left(\frac{T}{T_F}\right) - \frac{\pi^2}{10}\left(\frac{T}{T_F}\right)^3 + O(T^5)\right] \tag{25}$$

$$\Delta H_{0\to T} = \int_0^T C_p(u)\, du$$
$$= \frac{\pi^2}{2}R\left[\frac{T^2}{2T_F} - \frac{3\pi^2}{40}\frac{T^4}{T_F^3} + O(T^6)\right] \tag{26}$$

$$\Delta G_{0\to T} = \Delta H_{0\to T} - TS(T) \tag{27}$$

$$= -\frac{\pi^2}{2}R\left[\frac{T^2}{2T_F} - \frac{\pi^2}{40}\frac{T^4}{T_F^3} + O(T^6)\right] \tag{28}$$

The set of eqs 22−28 shows that at very low temperatures ($T \to 0$), one may expect

$$U(T) = \frac{3}{5}N\varepsilon_F = Cte \tag{29}$$

$$C_p(T) = S(T) \tag{30}$$

$$\Delta G_{0\to 1} = -\Delta H_{0\to T} \tag{31}$$

within absolute errors in the order of $O(T^2)$, $O(T^3)$, and $O(T^4)$, respectively. This would be an interesting test point for computed data. Now, what is special when the gas is rather completely nondegenerated?

**2.2. Case of the Completely Nondegenerated Gas ($a \to 0$).** In this case, $a \to 0$ and corresponds to $T \to \infty$. Thus, we have

$$f_p(a) \simeq a \tag{32}$$

Replacing this new equation (eq 32) into eq 12 leads to

$$a \simeq \frac{P^{\circ}h^3}{gk_{\mathrm{B}}(2\pi mk_{\mathrm{B}})^{3/2}T^{5/2}} \tag{33}$$

Equations 32 and 33 conjointly with eq 11 definitely give

$$S(T) \simeq \frac{5}{2}R + R\log\left[\frac{(2\pi mk_{\mathrm{B}}T)^{3/2}k_{\mathrm{B}}T}{P^{\circ}h^3}g\right] = S_{\mathrm{cl}}(T) \tag{34}$$

which is the Sackur−Tetrode equation for a classical gas. Thus, at very high temperatures, the quantum gas can be described excellently as a classical gas that follows the Boltzmann statistic.

Consequently, at extremely high temperatures ($T \to \infty$),

$$C_p(T) = \frac{5}{2}R \tag{35}$$

$$U(T) = \frac{3}{2}RT \tag{36}$$

$$\Delta H_{0\to T} = \frac{5}{2}RT \tag{37}$$

As a result, the classical limit can be appreciated at very high temperatures by the convergence of the functions $f_1, f_2, f_3$, and $f_4$ defined by

$$f_1(T) = |S(T) - S_{\mathrm{cl}}(T)| \tag{38}$$

$$f_2(T) = \left|\frac{2}{5}C_P(T) - R\right| \tag{39}$$

$$f_3(T) = \left|\frac{2}{3}\frac{U(T + \Delta T) - U(T)}{\Delta T} - R\right| \tag{40}$$

$$f_4(T) = \left|\frac{2}{5}\frac{\Delta H_{0\to T+\Delta T} - \Delta H_{0\to T}}{\Delta T} - R\right| \tag{41}$$

This would be an additional interesting test point for computed data. In addition, eq 35 indicates that the heat capacity converges to $5R/2$ at high temperatures. This value is the highest value of the heat capacity. Therefore, the discrete values of the heat capacity form an increasing series at least at high temperatures, because the series is convergent.

## 3. COMPUTATIONAL DETAILS

In this section, we provide all details related to numerical methods used for derivation or integration. We also discuss the accuracy of our results regarding the suitable cutoff value for the calculated temperature and its step size.

**3.1. Numerical Methods and Precision.** Equations 5, 11, and 12 were used conjointly to determine the entropy of the proton. In these equations, the Fermi integrals were performed using the Romberg integration method within an absolute error of $1.0 \times 10^{-15}$ units. We noted that higher precision for the integration does not change the computed temperature within its absolute error ($\delta T = 10^{-9}$ K), which is discussed in the next section. Moreover, the upper limit of the integration in the expression of Fermi integrals has been determined through the vanishing point of the difference between two successive integrations.

The heat capacity, the integrated heat capacity, and the Gibbs free energy change are computed using the following definitions

$$C_P(T) = T\left(\frac{\partial S}{\partial T}\right)_P \tag{42}$$

$$\Delta H_{0\to T} = \int_0^T C_P(u)\,\mathrm{d}u \tag{43}$$

$$\Delta G_{0\to T} = \Delta H_{0\to T} - TS(T) \tag{44}$$

respectively.

One can also note that the entropy of the proton is a regular function of the temperature. Thus, 3-point or 5-point differentiation method could be enough to handle the heat capacities from entropy data. Both methods gave exactly the same results. It is important to note that the integrated heat capacity is computed using the Simpson rule, which is the highest level integration method for equally spaced discrete data.

Therefore, aiming to improve earlier results[27,28] and to provide accurate data at all temperatures without calling data interpolation, we started looking for a reliable cutoff value and step size for the estimated temperatures. Of course, these parameters depend neither on the pressure nor on the proton spin, which are constants in the expression of the temperature (eq 12). So, the tests were performed at 1 atm, without taking into account the proton spin. Thus, derived conclusions are also valid whatever the pressure and whatever the assigned proton spin degeneracy.

**3.2. Cutoff Value for the Estimated Temperature.** The cutoff value for the estimated temperature is defined here as the absolute error with the estimated temperature known from eq 12. The lower this value is, the more accurate results are, and the higher the computational time is. The best compromise between the computational time and the accuracy is evaluated here. We computed the thermodynamic parameters of the proton at extremely low and high temperatures, with various cutoff values of $\delta T = 10^{-2}, 10^{-3}, 10^{-4}, 4 \times 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7}, 10^{-8}, 10^{-9}, 10^{-10}$, and $10^{-11}$. For all temperatures investigated, all the TPP converge as the cutoff value decreases (Table S1, Supporting Information).[40] Remark that the cutoff value of $4 \times 10^{-4}$ K (the one used by Bartmess)[27] leads to a low accuracy in results. Note also that within four decimal significant figures, the entropy and the heat capacity converge for $\delta T = 10^{-6}$ K. Even the integrated heat capacity and Gibbs free energy change converge for this value of $\delta T$. Thus, one would retain a cutoff value of $10^{-6}$ K to expect an accuracy at least within four decimal significant figures. To check the reliability of the latter cutoff value, we undertook calculations of errors on TPP for $T = 0.01-10$ K, within this cutoff value. Two issues were reported after that. The first one is that the relative error on integrated heat capacity and Gibbs free energy change is about 20% at 0.01 K. This relative error is too high and cannot be accepted. The errors on computed data were calculated using formulas defined in the Supporting Information.[40] The other issue lay on the calculated absolue error on the heat capacity. This parameter increases and reaches the value of 0.0020 J mol$^{-1}$ around 10 K. Note that this error is very high, as compared to the expected accuracy within four decimal significant figures (at least). In addition, this high deviation may lead to oscillations values of the heat capacity at high temperatures. In fact, farther in this work, the calculated heat capacities do show that the increment of the heat capacity is less than 0.0001 J mol$^{-1}$, for $T \geq 25$ K.

**Table 1. Computed Entropies, Heat Capacities, Integrated Heat Capacities, and Gibbs Free Energies Changes of the Free Proton in Gas Phase and at the Standard Pressure (1 bar)[a,b]**

| $T$ | $S$ | | $C_P$ | | $\Delta H_{0 \to T}$ | | $\Delta G_{0 \to T}$ | |
|---|---|---|---|---|---|---|---|---|
| | classic | quantum | classic | quantum | classic | quantum | classic | quantum |
| 0.0000 | $-\infty$ | 0.0000 | 0.0000 | 0.0000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| 0.0100 | −105.2093 | 0.0592 | 20.7862 | 0.0592 | 0.00020 | 0.00000 | 0.00126 | −0.00000 |
| 0.0500 | −71.7553 | 0.2958 | 20.7862 | 0.2958 | 0.00104 | 0.00001 | 0.00463 | −0.00001 |
| 0.1000 | −57.3474 | 0.5916 | 20.7862 | 0.5918 | 0.00208 | 0.00003 | 0.00781 | −0.00003 |
| 0.2000 | −42.9396 | 1.1837 | 20.7862 | 1.1850 | 0.00416 | 0.00019 | 0.01275 | −0.00019 |
| 0.5000 | −23.8934 | 2.9671 | 20.7862 | 2.9840 | 0.01039 | 0.00074 | 0.02234 | −0.00074 |
| 1.0000 | −9.4855 | 5.9642 | 20.7862 | 5.9919 | 0.0208 | 0.0030 | 0.0303 | −0.0030 |
| 2.0000 | 4.9223 | 11.7570 | 20.7862 | 11.0189 | 0.0416 | 0.0116 | 0.0317 | −0.0119 |
| 5.0000 | 23.9685 | 25.2607 | 20.7862 | 17.9778 | 0.1039 | 0.0574 | −0.0159 | −0.0689 |
| 10.0000 | 38.3764 | 38.6342 | 20.7862 | 20.1606 | 0.2079 | 0.1545 | −0.1759 | −0.2318 |
| 20.0000 | 52.7842 | 52.8309 | 20.7862 | 20.6700 | 0.4157 | 0.3596 | −0.6310 | −0.6970 |
| 50.0000 | 71.8304 | 71.8351 | 20.7862 | 20.7743 | 1.0393 | 0.9820 | −2.5522 | −2.6097 |
| 100.0000 | 86.2382 | 86.2391 | 20.7862 | 20.7841 | 2.0786 | 2.0211 | −6.5452 | −6.6028 |
| 150.0000 | 94.6663 | 94.6666 | 20.7862 | 20.7854 | 3.1179 | 3.0603 | −11.0820 | −11.1397 |
| 200.0000 | 100.6461 | 100.6463 | 20.7862 | 20.7858 | 4.1572 | 4.0996 | −15.9720 | −16.0296 |
| 250.0000 | 105.2844 | 105.2845 | 20.7862 | 20.7859 | 5.1965 | 5.1389 | −21.1246 | −21.1822 |
| 273.1500 | 107.1252 | 107.1253 | 20.7862 | 20.7860 | 5.6777 | 5.6201 | −23.5835 | −23.6412 |
| 298.1500 | 108.9456 | 108.9456 | 20.7862 | 20.7860 | 6.1974 | 6.1398 | −26.2847 | −26.3424 |
| 300.0000 | 109.0742 | 109.0742 | 20.7862 | 20.7860 | 6.2358 | 6.1782 | −26.4864 | −26.5441 |
| 350.0000 | 112.2784 | 112.2784 | 20.7862 | 20.7861 | 7.2752 | 7.2175 | −32.0223 | −32.0799 |
| 400.0000 | 115.0540 | 115.0540 | 20.7862 | 20.7861 | 8.3145 | 8.2568 | −37.7071 | −37.7648 |

[a]Here, the proton spin degeneracy is not taken into account, as recommended by the thermochemical conventions. [b]The calculated values of the entropy were obtained using an iterative and self-consistent procedure based on eqs 5 and 12 where the parameter $a$ is unknown. Those of the other thermodynamic parameters were obtained by differentiation or integration of data. Classic and quantum thermodynamic data are related to Boltzmann and Fermi−Dirac statistics, respectively. The entropy and heat capacity are given in J mol$^{-1}$ K$^{-1}$, whrereas the enthalpy and free energy are given in kJ mol$^{-1}$.

As a result, using a cutoff value of $10^{-6}$ K or higher is not suitable to expect reliable and high accurate results. Consequently, to ensure a better compromise between the computational time and the accuracy of results, we chose the lowest cutoff value ($10^{-9}$ K) from which all the calculated thermodynamic parameters converge at least within eight decimal significant figures. With this new cutoff value, we obtained a serendipitous precision of 0.02%, for the integrated heat capacity and the Gibbs free energy change at $T = 0.01-10$ K. As for the absolute error on the heat capacity, it is now about $2 \times 10^{-6}$ J mol$^{-1}$ around 10 K. This value, which is lower than the expected accuracy, does not change notably at higher temperatures. The very low relative and absolute errors obtained on the computed TPP with $\delta T = 10^{-9}$ K, make this cutoff value suitable for further computations.

**3.3. Temperature Step Size.** The reliable temperature step size is very useful to expect high accuracy on heat capacities, integrated heat capacities and Gibbs free energy changes. Thus, we undertook computations at some low, medium, and high temperatures, with the step sizes of $\Delta T = 10^{0}$, $10^{-1}$, $10^{-2}$, $10^{-3}$, $10^{-4}$, and $10^{-5}$ K, for each of these temperatures (Table S2, Supporting Information).[40]

For $T \geq 200$, the heat capacities calculated with the step size of $10^{-5}$ K is higher than 20.78616 J mol$^{-1}$. This value, which corresponds to $2.5R$, is the highest possible value of the heat capacity of a free particles gas. This is an indication that the step size used may be too low and thereafter may lead to considerable computational errors. To sustain this statement, we redid computations at 300 and 400 K with the step size of $10^{-6}$ and $10^{-7}$ K. As a result, the heat capacity calculated at 300 K with each of these step sizes is higher than the one calculated

at 400 K. Such results are inconsistent with the fact that the heat capacity of a free quantum gas should be a strictly increasing function of the temperature. Thus, doing computations with a temperature step size lower or equals $10^{-5}$ K would lead to erratic computational errors and inaccurate results.

Elsewhere, we can remark the convergence of the heat capacity for $\Delta T = 10^{-4}$ K. This threshold can be brought up to $10^{-2}$ K, reporting the accuracy of the heat capacity within four decimal significant figures. Note the unchanged values of the integrated heat capacity and Gibbs free energy change, from $\Delta T = 10^{-4}$ to $10^{-2}$ K at low temperatures. Therefore, the step size of $10^{-2}$ K could ensure a better compromise between the computational time and the accuracy of results. As a result, throughout this work, heat capacities and integrated heat capacities were computed with a temperature step size of $10^{-2}$ K.

## 4. RESULTS AND DISCUSSION

Once the cutoff value and the step size for the estimated temperature were determined thoroughly, all the TPP were computed for $T = 0-400$ K at 1 bar and 1 atm of pressure. That is, eqs 5, 11, and 12 were evaluated conjointly for each of these pressures. As nuclear spins are not altered in chemical reactions, the thermochemical convention ignores the nuclear spin. Thus, to make our results fit in this convention, we did calculations of TPP, ignoring the proton degeneracy. For the sake of generality, we also computed TPP by taking into account the proton spin degeneracy, which is normal for nuclear reactions.

**4.1. TPP without the Proton Spin Degeneracy ($g = 1$).** Nowadays, the standard pressure is 1 bar. However, several

researchers still undertake experiment or calculations at a pressure of 1 atm. Moreover, several computational physics or chemistry codes assume the default pressure to be 1 atm. For all these reasons, we undertook calculations at both pressures.

*4.1.1. Data at the Standard Pressure (1 bar).* In this section, we present the calculated TPP in the standard pressure and for $T = 0-400$ K. The proton spin degeneracy is not taken into account here. Table 1 reports data at some temperatures. Data at all temperatures involved were collected in Figure 1 and
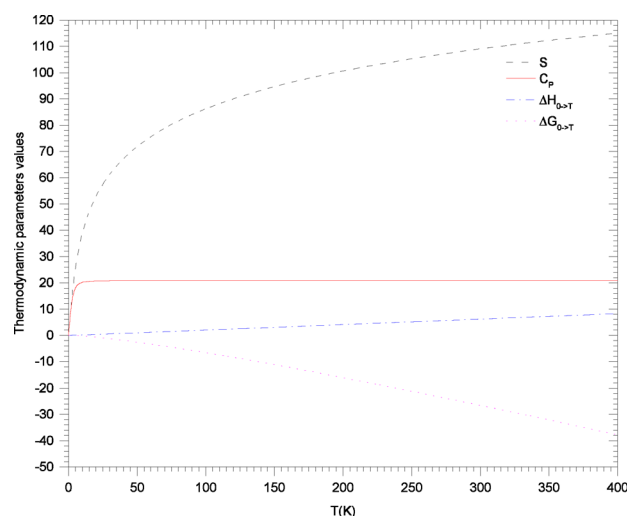


**Figure 1.** Plot of the calculated entropy ($S$), heat capacity ($C_P$), integrated heat capacity ($\Delta H_{0 \to T}$), and Gibbs free energy change ($\Delta G_{0 \to T}$) of the proton in the gas phase, for temperatures ranging from 0 to 400 K at 1 bar. $S$ and $C_P$ are given in J mol$^{-1}$ K$^{-1}$, and $\Delta H_{0 \to T}$ and $\Delta G_{0 \to T}$ are in kJ mol$^{-1}$.

Table S3 (Supporting Information). We can note that at extremely low temperatures, we do have $S(T) = C_P(T)$ and $\Delta H_{0 \to T} = \Delta G_{0 \to T}$, as expected by the theory. Moreover, the classical limit is really appreciated at high temperatures through the convergence of the functions $f_1, f_2, f_3$ and $f_4$ defined in the subsection 2.2. The strict convergence of these functions is noted at $T \geq 200$ K, within an absolute error lower than 0.0001 units (Table S4, Supporting Information).[40] Thus, the free proton gas can be assumed to be classical at temperatures higher than 200 K, with an excellent precision. As a matter of fact, the classical assumption depends on the fixed uncertainty on thermodynamic data. However, it is important to note that quantum effects on the gas phase proton motion is really significant at low temperatures ($T \leq 120$ K) (Table S4, Supporting Information).[40] We can also appreciate the strict increase of the heat capacity with the temperature, as expected by the theory. The tests points achieved at very low and very high temperatures are enough to validate the results obtained through our computations.

We can also note that, although quantum effects on the TPP are really significant at temperatures lower than 120 K, they cover a large range of temperatures from 0 to $10^4$ K in the case of the free electron.[41] This is due to the difference of mass between these two particles, as the electron is very light as compared to the proton.

Although the proton behaves as a classical particle at high temperatures, we strongly recommend the use of quantum results at all temperatures for the integrated heat capacity and the Gibbs free energy change. The reason for this

recommendation is that these thermodynamic parameters depend on all successive values at previous temperatures in which the proton gas was strongly degenerated.

Interestingly, our results at 1 bar are very close to those published earlier by Bartmess,[27,28] except for the heat capacities. For the entropies, the integrated heat capacities and the Gibbs free energies changes, the discrepancies are only about 0.0009 J mol$^{-1}$ K, 0.0005 kJ mol$^{-1}$, and 0.0005 kJ mol$^{-1}$, respectively. The percentage errors on the heat capacities provided by Bartmess[27,28] are very high. They are about 3−50% at very low temperatures ($T \leq 5$ K). At higher temperatures, the mean absolute error on his heat capacities is about 0.0070 J mol$^{-1}$ K$^{-1}$, which is too high as compared to the heat capacity increment at these temperatures and then may explain the oscillating values obtained by Bartmess. Consequently, we advise the use of the improved results for future investigations at a pressure of 1 bar.

*4.1.2. Thermodynamic Data at 1 atm.* Some computed data at 1 atm were reported in Table 2. Data at all temperatures involved were shifted to Table S5 (Supporting Information). Even at this pressure, the free proton gas can be assumed to be classical for temperatures higher than 200 K. From these data, we can also appreciate all the features noted previously in data at 1 bar. The little change of pressure from 1 bar to 1 atm notably affects the entropy and Gibbs free energy change. The highest effects (about 0.11 J mol$^{-1}$ K for the entropy and −0.04 kJ mol$^{-1}$ K for the Gibbs free energy change) were noted at high temperatures ($T \geq 200$ K). The heat capacity and the integrated heat capacity are not generally affected by this slight pressure change, except at low temperatures ($T \leq 20$ K) were the change in the heat capacity is at most 0.04 J mol$^{-1}$ K.

Even though the change in pressure is little, for the sake of accuracy, we always recommend the use of data collected at the same pressure as that undertaken in calculations or experiments.

**4.2. TPP with the Proton's Spin Degeneracy On.** For the sake of generality, we took into account the proton's spin degeneracy and reported the TPP in the standard pressure for $T = 0-400$ K. The results obtained were summarized in Table S6 (Supporting Information).[40] Note that the same features reported at extremely and high temperatures when the proton spin was not taken into account are also noted here. In addition, in this case in which the proton's spin is taken into account, the free proton gas is classical for $T > 150$ K.

## 5. CONCLUSION

In this work, the thermodynamics of the free proton in gas phase was revised at all temperatures in the standard pressure (1 bar). New data were also provided at 1 atm of pressure. The proton in the gas phase was treated as a particle of an ideal gas and described in a grand canonical ensemble. Its thermodynamics was undertaken by assuming it as a classical particle in a first approach and, as a quantum particle in the second approach. The first approach is based on the Boltzmann formalism, and the second is based on the Fermi−Dirac formalism, which involves a self-consistent iterative procedure for temperatures ranging from 0 to 400 K.

It comes out that our results are highly accurate and could be recommended for future investigations. Interestingly, the free proton gas can be assumed to be classical for temperatures higher than 200 K, with an excellent precision. However, it is worth mentioning that quantum effects on the gas phase proton motion is really significant at low temperatures ($T \leq 120$ K).

**Table 2. Computed Entropies, Heat Capacities, Integrated Heat Capacities, and Gibbs Free Energies of the Free Proton in Gas Phase and at the Standard Pressure (1 atm)[a,b]**

| | $S$ | | $C_P$ | | $\Delta H_{0 \to T}$ | | $\Delta G_{0 \to T}$ | |
|---|---|---|---|---|---|---|---|---|
| $T$ | classic | quantum | classic | quantum | classic | quantum | classic | quantum |
| 0.0000 | $-\infty$ | 0.0000 | 0.0000 | 0.0000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| 0.0100 | −105.3188 | 0.0588 | 20.7862 | 0.0588 | 0.00020 | 0.00000 | 0.00126 | −0.00000 |
| 0.0500 | −71.8647 | 0.2942 | 20.7862 | 0.2943 | 0.00104 | 0.00000 | 0.00463 | −0.00000 |
| 0.1000 | −57.4569 | 0.5885 | 20.7862 | 0.5887 | 0.00208 | 0.00003 | 0.00781 | −0.00003 |
| 0.2000 | −43.0490 | 1.1775 | 20.7862 | 1.1788 | 0.00416 | 0.00012 | 0.01275 | −0.00012 |
| 0.5000 | −24.0029 | 2.9514 | 20.7862 | 2.9681 | 0.01039 | 0.00074 | 0.02234 | −0.00074 |
| 1.0000 | −9.5950 | 5.9327 | 20.7862 | 5.9612 | 0.0208 | 0.0030 | 0.0303 | −0.0030 |
| 2.0000 | 4.8129 | 11.6991 | 20.7862 | 10.9750 | 0.0416 | 0.0116 | 0.0317 | −0.0118 |
| 5.0000 | 23.8590 | 25.1661 | 20.7862 | 17.9497 | 0.1039 | 0.0573 | −0.0159 | −0.0686 |
| 10.0000 | 38.2669 | 38.5281 | 20.7862 | 20.1528 | 0.2079 | 0.1543 | −0.1759 | −0.2310 |
| 20.0000 | 52.6748 | 52.7221 | 20.7862 | 20.6685 | 0.4157 | 0.3593 | −0.6310 | −0.6951 |
| 50.0000 | 71.7209 | 71.7257 | 20.7862 | 20.7741 | 1.0393 | 0.9817 | −2.5522 | −2.6046 |
| 100.0000 | 86.1288 | 86.1297 | 20.7862 | 20.7840 | 2.0786 | 2.0208 | −6.5452 | −6.5922 |
| 150.0000 | 94.5569 | 94.5572 | 20.7862 | 20.7854 | 3.1179 | 3.0600 | −11.0820 | −11.1235 |
| 200.0000 | 100.5367 | 100.5368 | 20.7862 | 20.7858 | 4.1572 | 4.0993 | −15.9720 | −16.0081 |
| 250.0000 | 105.1750 | 105.1750 | 20.7862 | 20.7859 | 5.1965 | 5.1386 | −21.1246 | −21.1552 |
| 273.1500 | 107.0158 | 107.0159 | 20.7862 | 20.7860 | 5.6777 | 5.6198 | −23.5835 | −23.6116 |
| 298.1500 | 108.8361 | 108.8362 | 20.7862 | 20.7860 | 6.1974 | 6.1394 | −26.2847 | −26.3101 |
| 300.0000 | 108.9647 | 108.9648 | 20.7862 | 20.7860 | 6.2358 | 6.1779 | −26.4864 | −26.5115 |
| 350.0000 | 112.1689 | 112.1690 | 20.7862 | 20.7861 | 7.2752 | 7.2172 | −32.0223 | −32.0419 |
| 400.0000 | 114.9445 | 114.9446 | 20.7862 | 20.7861 | 8.3145 | 8.2565 | −37.7071 | −37.7213 |

[a]Here, the proton spin degeneracy is not taken into account, as recommended by the thermochemical conventions. [b]The calculated values of the entropy were obtained using an iterative and self-consistent procedure based on eqs 5 and 12 where the parameter $a$ is unknown. Those of the other thermodynamic parameters were obtained by differentiation or integration of data. Classic and quantum thermodynamic data are related to Boltzmann and Fermi−Dirac statistics, respectively. The entropy and heat capacity are given in J mol$^{-1}$ K$^{-1}$, whrereas the enthalpy and free energy are given in kJ mol$^{-1}$.

Elsewhere, although the proton behaves as a classical particle at high temperatures, we strongly recommend the use of quantum results at all temperatures, for the integrated heat capacity and the Gibbs free energy change. The reason for this recommendation is that these thermodynamic parameters depend on all successive values at previous temperatures in which the proton gas was strongly degenerated.

It is also useful to note that the little change of the pressure from 1 bar to 1 atm affects notably the entropy and the Gibbs free energy change of the proton. Thus, we advise the use of data related to the same pressure as in the experiment or in all calculations involving the gas phase proton. Doing this will preserve the accuracy on thermodynamic quantities evaluated. Therefore, explicit pressure effects would be prominent and would enhance the accuracy on thermodynamic quantities evaluated at many other pressures.

## ASSOCIATED CONTENT

**S** Supporting Information

Calculation of absolute and relative errors. Completed tables of TPP data and $f$ function values computed at various temperatures, at pressures of 1 bar and 1 atm, with and without proton spin degeneracy. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

**Corresponding Author**

*J. J. Fifen. E-mail: julesfifen@gmail.com. Tel: 00237 7521 6139.

**Notes**

The authors declare no competing financial interest.

## REFERENCES

(1) Liptak, M. D.; Shields, G. C. Accurate pKa Calculations for Carboxylic Acids Using Complete Basis Set and Gaussian-n Models Combined with CPCM Continuum Solvation Methods. *J. Am. Chem. Soc.* **2001**, *123*, 7314−7319.

(2) Guimares, C. R. W.; Bicca de Alencastro, R. Evaluating the Relative Free Energy of Hydration of New Thrombin Inhibitor Candidates Using the Finite Difference Thermodynamic Integration (FDTI) Method. *Int. J. Quantum Chem.* **2001**, *85*, 713−726.

(3) Liptak, M. D.; Gross, K. C.; Seybold, P. G.; Feldgus, S.; Shields, G. C. Absolute pKa Determinations for Substituted Phenols. *J. Am. Chem. Soc.* **2002**, *124*, 6421−6427.

(4) Range, K.; Riccardi, D.; Cui, Q.; Elstner, M.; York, D. M. Benchmark Calculations of Proton Affinities and Gas-Phase Basicities of Molecules Important in the Study of Biological Phosphoryl Transfer. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3070−3079.

(5) Riccardi, D.; Schaefer, P.; Cui, Q. pKa Calculations in Solution and Proteins with QM/MM Free Energy Perturbation Simulations:? A Quantitative Test of QM/MM Protocols. *J. Phys. Chem. B* **2005**, *109*, 17715−17733.

(6) Holland, J. P.; Green, J. C.; Dilworth, J. R. Probing the Mechanism of Hypoxia Selectivity of Copper Bis-(Thiosemicarbazonato) Complexes: Dft Calculation of Redox Potentials and Absolute Acidities in Solution. *Dalton Trans.* **2006**, 783−794.

(7) Ho, J.; Coote, M. L. pKa Calculation of Some Biologically Important Carbon Acids - An Assessment of Contemporary Theoretical Procedures. *J. Chem. Theory Comput.* **2009**, *5*, 295−306.

(8) Surawatanawong, P.; Tye, J. W.; Darensbourg, M. Y.; Hall, M. B. Mechanism of Electrocatalytic Hydrogen Production by a Di-Iron Model of Iron-Iron Hydrogenase: A Density Functional Theory Study of Proton Dissociation Constants and Electrode Reduction Potentials. *Dalton Trans.* **2010**, *39*, 3093−3104.

(9) Bouchoux, G.; Huang, S.; Inda, B. S. Acid-Base Thermochemistry of Gaseous Aliphatic α-Aminoacids. *Phys. Chem. Chem. Phys.* **2011**, *13*, 651−668.

(10) Ali-Torres, J.; Rodriguez-Santiago, L.; Sodupe, M. Computational Calculations of pKa Values of Imidazole in Cu(II) Complexes of Biological Relevance. *Phys. Chem. Chem. Phys.* **2011**, *13*, 7852−7861.

(11) Rebollar-Zepeda, A. M.; Campos-Hernandez, T.; Ramirez-Silva, M. T.; Rojas-Hernandez, A.; Galano, A. Searching for Computational Strategies to Accurately Predict pKas of Large Phenolic Derivatives. *J. Chem. Theory Comput.* **2011**, *7*, 2528−2538.

(12) Riffet, V.; Frison, G.; Bouchoux, G. Acid-Base Thermochemistry of Gaseous Oxygen and Sulfur Substituted Amino Acids (Ser, Thr, Cys, Met). *Phys. Chem. Chem. Phys.* **2011**, *13*, 18561−18580.

(13) Fifen, J. J.; Nsangou, M.; Dhaouadi, Z.; Motapon, O.; Jaidane, N. Solvent Effects on the Antioxidant Activity of 3,4-Dihydroxyphenylpyruvic Acid: {DFT} and TD-DFT Studies. *Comput. Theor. Chem.* **2011**, *966*, 232−243.

(14) Najafi, M.; Zahedi, M.; Klein, E. DFT/B3LYP Study of the Solvent Effect on the Reaction Enthalpies of Homolytic and Heterolytic {OH} Bond Cleavage in Mono-Substituted Chromans. *Comput. Theor. Chem.* **2011**, *978*, 16−28.

(15) Altarawneh, M.; Dar, T.; Dlugogorski, B. Z. Thermochemical Parameters and pKa Values for Chlorinated Congeners of Thiophenol. *J. Chem. Eng. Data* **2012**, *57*, 1834−1842.

(16) Marenich, A. V.; Ding, W.; Cramer, C. J.; Truhlar, D. G. Resolution of a Challenge for Solvation Modeling: Calculation of Dicarboxylic Acid Dissociation Constants Using Mixed DiscreteContinuum Solvation Models. *J. Phys. Chem. Lett.* **2012**, *3*, 1437−1442.

(17) Gupta, M.; da Silva, E. F.; Svendsen, H. F. Modeling Temperature Dependency of Amine Basicity Using PCM and SM8T Implicit Solvation Models. *J. Phys. Chem. B* **2012**, *116*, 1865−1875.

(18) Abedi, M.; Farrokhpour, H. Acidity Constants of Some Sulfur Oxoacids in Aqueous Solution Using CCSD and MP2 Methods. *Dalton Trans.* **2013**, *42*, 5566−5572.

(19) Houari, Y.; Jacquemin, D.; Laurent, A. D. Methodological Keys for Accurate Simulations. *Phys. Chem. Chem. Phys.* **2013**, *15*, 11875−11882.

(20) Psciuk, B. T.; Schlegel, H. B. Computational Prediction of One-Electron Reduction Potentials and Acid Dissociation Constants for Guanine Oxidation Intermediates and Products. *J. Phys. Chem. B* **2013**, *117*, 9518−9531.

(21) Fifen, J. J.; Nsangou, M.; Dhaouadi, Z.; Motapon, O.; Jaidane, N.-E. Solvation Energies of the Proton in Methanol. *J. Chem. Theory Comput.* **2013**, *9*, 1173−1181.

(22) Mazzone, G.; Toscano, M.; Russo, N. Density Functional Predictions of Antioxidant Activity and UV Spectral Features of Nasutin A, Isonasutin, Ellagic Acid, and One of Its Possible Derivatives. *J. Agric. Food Chem.* **2013**, *61*, 9650−9657.

(23) Marenich, A. V.; Ho, J.; Coote, M. L.; Cramer, C. J.; Truhlar, D. G. Computational Electrochemistry: Prediction of Liquid-Phase Reduction Potentials. *Phys. Chem. Chem. Phys.* **2014**, *16*, 15068−15106.

(24) Fermi, E. Zur Quanteling des Idealen Einatomigen Gases. *Z. Phys.* **1926**, *36*, 902−912.

(25) Sommerfeld, A. Zur Elektronentheories der Metalle auf Grund der Fermischen Statistik. *Z. Phys.* **1928**, *47*, 1−32.

(26) Lewis, G. N.; Gibson, G. E.; Latimer, W. M. A Revision of the Entropies of the Elements. *J. Am. Chem. Soc.* **1922**, *44*, 1008−1017.

(27) Bartmess, J. E. Thermodynamics of the Electron and the Proton. *J. Phys. Chem.* **1994**, *98*, 6420−6424.

(28) Bartmess, J. E. Thermodynamics of the Electron and the Proton [Erratum to document cited in CA121:19495]. *J. Phys. Chem.* **1995**, *99*, 6755.

(29) Mitchell, A. C. G. Entropie Des Elektronengases auf Grund der Fermischen Statistik. *Z. Phys.* **1928**, *51*, 720−725.

(30) http://physics.nist.gov/cuu/Constants/.

(31) Mohr, P. J.; Taylor, B. N.; Newell, D. B. CODATA Recommended Values of the Fundamental Physical Constants: 2010a). *J. Phys. Chem. Ref. Data* **2012**, *41*, −.

(32) McDougall, J.; Stoner, E. C. The Computation of Fermi−Dirac Functions. *Phyl. Trans. R. Soc. London A* **1938**, *237*, 67−104.

(33) Joyce, W. B.; Dixon, R. W. Analytic Approximations for the Fermi Energy of an Ideal Fermi Gas. *Appl. Phys. Lett.* **1977**, *31*, 354−356.

(34) Blakemore, J. Approximations for Fermi−Dirac Integrals, Especially the Function $F_{1/2}(\eta)$ Used to Describe Electron Density in a Semiconductor. *Solid-State Electron.* **1982**, *25*, 1067−1076.

(35) Aguilera-Navarro, V. C.; Estvez, G. A.; Kostecki, A. A Note on the Fermi-Dirac Integral Function. *J. Appl. Phys.* **1988**, *63*, 2848−2850.

(36) Wong, S. A.; McAlister, S. P.; Li, Z.-M. A Comparison of Some Approximations for the Fermi−Dirac Integral of Order 1/2. *Solid-State Electron.* **1994**, *37*, 61−64.

(37) Selvaggi, J. A.; Selvaggi, J. P. The Analytical Evaluation of the Half-Order Fremi-Dirac Integrals. *Open Math. J.* **2012**, *5*, 1−7.

(38) Fukushima, T. Analytical Computation of Generalized Fermi-Dirac Integrals by Truncated Sommerfeld Expansions. *Appl. Math. Comput.* **2014**, *234*, 417−433.

(39) Fukushima, T. Computation of a General Integral of Fermi-Dirac Distribution by Mcdougall-Stoner Method. *Appl. Math. Comput.* **2014**, *238*, 485−510.

(40) See Supporting Information.

(41) Fifen, J. J. Thermodynamics of the Electron Revisited and Generalized. *J. Chem. Theory Comput.* **2013**, *9*, 3165−3169.