

Thermodynamics of the Electron and the Proton

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The currently accepted conventions for the thermodynamics of the electron do not follow the proper statistical mechanics equations. The correct values are here obtained from numerical solution of the Fermi–Dirac statistical mechanics equations, yielding an entropy at 298.15 K of 22.734 J/mol·K (5.434 cal/mol·K) and an integrated heat capacity at the same temperature of 3.145 kJ/mol·K (0.752 kcal/mol). The effect that this would have, based on the current thermochemical conventions, on the thermodynamics of the proton, and of all other gaseous ions, is noted.

The amount of thermochemical data known for gas-phase ions has greatly increased in recent years.^{1–6} Such data come from a variety of sources including ionization and appearance energies, which yield ionic thermochemical values relative to the neutral species' thermochemistry, and ion/molecule reactions, which yield values relative to both other ions' and neutral species' values. Although for many purposes such relative values are acceptable, converting the data to the best enthalpies and free energies of formation possible is still a desirable goal. This is both for scientific accuracy and for a general aesthetic sense of the completeness of science.

All of gas-phase ion thermochemistry is based on the values for the thermochemistry of the electron. It is obviously necessary for electron affinities



and also for ionization energies



These quantities are commonly measured as the (0, 0) threshold values, corresponding to 0 K. To convert these values to some higher temperature (typically 298 K) requires the integrated heat capacity $H_T - H_0$ for the various species involved. Reactions 1 and 2 can also be determined as relative values via ion/molecule equilibria, which yield the free energy differences. In this case, to obtain the enthalpy requires knowledge of the entropy S_T for the species involved.

The ionization energy of the hydrogen atom



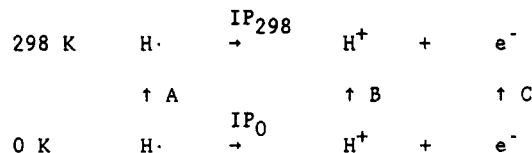
is a special case of eq 2. This, in combination with the thermochemistry of the hydrogen atom, yields the $\Delta_f H(H^+)$ and $\Delta_f G(H^+)$ necessary for obtaining absolute gas-phase basicities or acidities:



(or the enthalpic equivalents, the proton affinity, and anion proton affinity⁷), as well as $\Delta_f H(BH^+)$ and $\Delta_f H(A^-)$. Thus, the thermochemistry of the electron is an anchor point for all other ionic thermochemistry.

There are two conventions in use at present for describing the energetics of the electron. The "electron convention" (EC) is used in compilations such as the JANAF Tables³ and the NIST

SCHEME 1



Tech Note 270.⁴ The EC declares the electron to be equivalent to an element, with both $\Delta_f H$ and $\Delta_f G$ therefore defined as equal to zero at all temperatures. The integrated heat capacity $H_T - H_0$ is taken as that for an ideal gas, $5/2RT$, or 6.1973 kJ/mol at 298.15 K, by conventional statistical mechanics. The entropy S_T is likewise evaluated as that of an ideal gas, being 20.9790 J/mol·K at 298.15 K. This is due to translational entropy, from the Sackur–Tetrode equation (eq 6), plus a degeneracy of $G = 2$ for the free electron:

$$S_{tr} = \frac{5}{2}R + R \ln \left\{ \frac{(2\pi m_e k_B T)^{3/2} k_B G}{P^\circ h^3} \right\} \quad (6)$$

where h is Planck's constant, P° is the standard state pressure, k_B is the Boltzmann constant, and m_e is the electron rest mass. Values for these constants are taken from the 1986 CODATA tables.⁸

In contrast, the "ion convention" (IC) has been used in the "Gaseous Ion Energetics" compilation² and the GIANT Tables,^{5,6} as well as in most papers published on the subject of gas-phase ion thermochemistry. This similarly sets $\Delta_f H(e^-)$ as equal to zero at all temperatures, but $H_T - H_0$ is also defined as equal to zero at all temperatures. The entropy and $\Delta_f G$ are not clearly defined for this convention,⁵ but it seems reasonable that if the integrated heat capacity is zero, then C_p either must be negative at some temperatures and positive at others or must be zero everywhere. The latter is assumed here, with the implication that S_T must be zero also.

As a further point of confusion, the reference standard state pressure used in earlier compilations^{3,4a} was 1 atm (760 Torr) but is now 1 bar (750.06 Torr) in more recent work.^{2,4b,5,6} This change causes the entropy of all species, both ionic and neutral, to be greater by 0.1092 J/mol·K^{4b} than previously noted.

The fundamental difference between the two conventions can be described using the thermochemical cycle in Scheme 1 for ionization energies:⁹ where A , B , and C are the integrated heat capacities for taking H , H^+ , and e^- from 0 to 298 K. In both conventions, B is taken as that of an ideal monatomic gas, $5/2RT$. A is the same, plus an electronic factor, from standard Boltzmann statistical mechanics. In the IC, with $C = 0$, all the enthalpic change on raising the cation and electron to some higher

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temperature is assigned to the cation. In the EC, $C = 5/2RT$, and the electron is taken as just another chemical species.

Sharpe and Richardson¹⁰ have pointed out that at one specific temperature, 297 K, the numeric value for ΔG for the IE process (eq 2) in the EC is that same as that in the IC. The same is true for the EA process (eq 1). This convergence of numeric values occurs because, in the EC, TS_T for the electron happens to be numerically equal to $H_T - H_0$ at that temperature. In the IC, both are always the same, equal to zero.

Because the EC and the IC are conventions, rather than reality, either of these should be adequate for anchoring the rest of ionic thermochemistry. For the reactions 1 and 2, it does not matter which convention is used, as long as it is used consistently; the relative values stay the same. Recently, however, there have been thermochemical measurements made on gas-phase reactions with the electron as a reactant,¹¹ such as



Such reactions cannot be described properly unless the thermochemistry of the electron, relative to other species, is known accurately. Reaction 7 is exothermic by -4.2 ± 2.0 kJ/mol in the vicinity of 400 K.¹¹ On the basis of what appear to be reliable data for electron affinities and bond strengths,⁶ the IC predicts +5.0 kJ/mol, while the EC predicts -3.8 kJ/mol. Thus, determination of the proper thermochemistry is necessary for use in these cases.

Which convention, EC or IC, is preferable? It seems reasonable that the integrated heat capacity of the electron should be non-zero, because it is a real species with non-zero rest mass. Thus at face value, the EC is the more likely choice. There are two problems with the EC, however, in that other aspects of it do not reflect what we know of reality. First, through the use of the standard Sackur-Tetrode equation (eq 6) for translational entropy, it is found that the entropy of the electron becomes negative at $T < 109.2$ K and goes to negative infinity at 0 K. Actually, the latter is true of all species for this equation, but the temperature at which S_T becomes negative is 1.59 K for the proton and even lower for larger species. A more serious problem with the EC is that the electron should not obey the form of statistical mechanics used for most chemical species.

All elementary particles are classified as fermions (obeying Fermi-Dirac statistical mechanics), bosons (obeying Bose-Einstein statistical mechanics), or boltzons (obeying Boltzmann statistical mechanics). Fermions are indistinguishable particles, only one of which can occupy an energy state (i.e. half-integral spins). These obey eq 8 with $k = +1$, where g_i is the degeneracy of a given energy level, α is $-\mu/kT$ where μ is the chemical potential, and β_i is $1/k_B T$.

$$N_i = \frac{g_i}{e^{\alpha} e^{\beta_i} - k} \quad (8)$$

Examples are the electron and the proton. Bosons are indistinguishable particles with no constraints placed upon the occupancy on the energy levels (i.e. integral spins). These follow eq 8 with $k = -1$; the photon is the most common example. In practice, the statistical mechanics used to describe most chemical species follow eq 8 with $k = 0$; these are distinguishable particles called boltzons, following Boltzmann statistics.¹² At high temperatures and low pressures (i.e. dilute gases), where the number of thermally accessible states is much greater than the number of particles, the distributions based on the Fermi-Dirac and Bose-Einstein statistics for indistinguishable particles approach the Boltzmann distribution very closely. The "standard" formulas for thermodynamic functions of chemicals based on statistical mechanistic derivations are from the Boltzmann distribution.

As noted above, the electron is a fermion, and thus Fermi-Dirac statistical mechanics are the appropriate treatment to use.

This has been known since the 1920s.¹³⁻¹⁵ The general question has been addressed more recently in the literature of both physics¹⁶ and chemistry.¹⁷ In both the earliest¹³ and most recent work,^{16,17} it was recognized that Fermi-Dirac statistics were the appropriate ones to use, but the actual data given were from the more conventional Boltzmann statistics. The first valid mathematical treatment was in the 1920s. The equations for the entropy of the free electron were explicitly given by Mitchell,¹⁸ based on work by Sommerfeld:¹⁴

$$S = \frac{5}{2} R \frac{U_{3/2}}{U_{1/2}} - R \ln(A) \quad (9)$$

$$U_\rho = \frac{1}{\Gamma(\rho + 1)} \int \frac{u^\rho du}{\frac{1}{A} e^u + k} \quad \text{for } \rho = 1/2 \text{ and } 3/2 \quad (10)$$

where $u = \epsilon/k_B T$, ϵ is the energy of the increasing energy levels, $A = e^{-\alpha}$, α is as in eq 8, and $k = 1$ for Fermi-Dirac statistics. Also,¹⁸

$$PV = \frac{VGk_B T (2\pi m_e k_B T)^{3/2} U_{3/2}}{h^3} \quad (11)$$

The variable A represents the degeneracy of the ensemble of electrons. It is related to the free energy of 1 mol of particles and depends in an approximately inverse sense on temperature and electron density.¹⁴ Equation 10 is not analytically soluble for S as a function of T at all T . For $A \gg 1$ ($T < 100$ K), eq 10 asymptotically approaches a limit and can be explicitly integrated.^{14,18} For $A < 1$ ($T > 315$ K), such a direct solution does not converge. Mitchell¹⁸ expanded the integrand of eq 10 and integrated the series for a limited number of terms, to arrive at values of S_T for 315, 406, and 492 K (corresponding to $A = 1.00$, 0.50, and 0.30). By means of a short extrapolation, a value of $S_{298} = 22.72$ J/mol·K was obtained.

Similarly, Gordon¹⁹ obtained free energy values for the electron at $T > 225$ K, although they were not presented in an explicit ΔG versus T format. The $U_{1/2}$ and $U_{3/2}$ integrals tabulated therein agree quite well with those derived in this work.

To obtain the integrated heat capacity accurately requires values of S at many temperatures, especially in the region from 100 to 300 K not directly accessible by Mitchell's techniques. In the present work these have been obtained by numerical integration of eq 10. This was done using a Touch Systems 50 MHz 80486 computer and code written in Microsoft Fortran Version 3.2. The numerical integration was carried out by summing in steps of 0.000 05 for u out to a change in the summation of less than 1.0×10^{-15} (the rounding error limit of double precision floating point numbers in Fortran). The U values so obtained are the same to seven digits as for a step size of 0.000 01 at the same convergence limit.

We want the value of S_T at all integer temperatures up to 1000 K. To assign a temperature to a given value of A , rearrangement of eq 11 gives

$$T^{5/2} = \frac{P^\circ h^3}{Gk_B (2\pi m_e k_B)^{3/2} U_{3/2}} \quad (12)$$

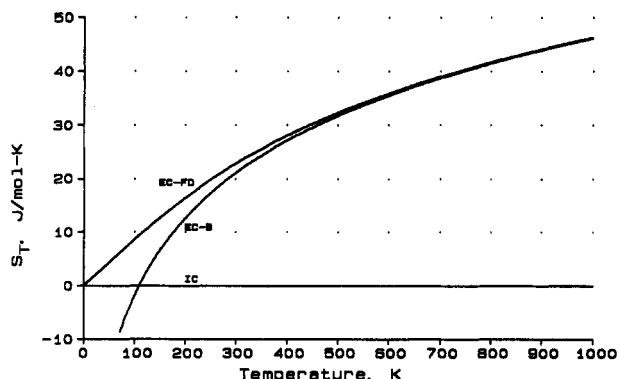
Equation 10 is evaluated as $U_{3/2}$ for a selected value of A , and then a temperature corresponding to that particular A is obtained from eq 12. The value of A is changed iteratively in eq 10 for $U_{3/2}$, until an A is obtained that gives a temperature within 0.0004 K of the desired integer T .

For these near-integer values of T from 1 to 1000 K, the A values are then used to evaluate $U_{1/2}$ and eq 9 is solved for S_T . The values of S_T obtained by this method for $T = 1-25$ K are linear with T ($r = 0.999\ 998$, slope = 0.08602 J/mol) with an

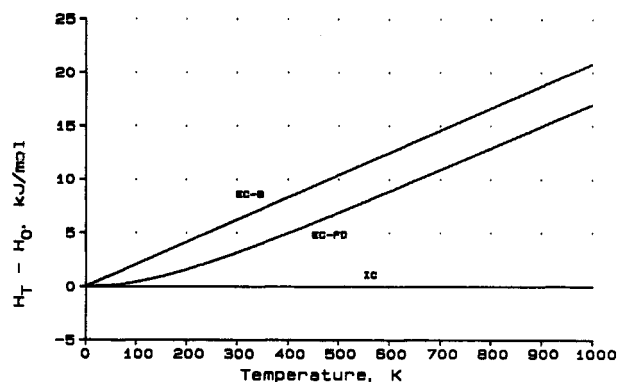
TABLE 1: Thermodynamics of the Electron by Fermi-Dirac Statistical Mechanics

T^a	S_T^b	C_p^c	E_T^d	$H_T - H_0^e$	A^f
1.00	0.0864	0.0733	0.0125	0.0000	0.745 52E+207
2.00	0.1724	0.1290	0.0250	0.0002	0.284 57E+104
5.00	0.4302	0.3872	0.0624	0.0011	0.259 52E+42
10.00	0.8594	0.8168	0.1247	0.0043	0.522 95E+21
20.00	1.7202	1.6806	0.2494	0.0172	0.211 57E+11
50.00	4.3209	4.3129	0.6236	0.1083	10 854.024
100.00	8.6457	8.4412	1.2472	0.4322	70.502 286
150.00	12.7299	11.7097	1.8708	0.9413	11.106 439
200.00	16.4574	14.1470	2.4944	1.5921	3.919 297
250.00	19.8188	15.9126	3.1179	2.3469	1.926 523
273.15	21.2576	16.5561	3.4067	2.7232	1.478 068
298.15	22.7337	17.1373	3.7185	3.1446	1.145 779
300.00	22.8398	17.1677	3.7415	3.1764	1.125 628
350.00	25.5584	18.0575	4.3651	4.0587	0.729 974
400.00	28.0141	18.6914	4.9887	4.9786	0.507 422
450.00	30.2439	19.1478	5.6123	5.9254	0.370 638
500.00	32.2799	19.4825	6.2359	6.8917	0.280 986
550.00	34.1493	19.7314	6.8595	7.8725	0.219 293
600.00	35.8749	19.9204	7.4831	8.8642	0.175 183
650.00	37.4757	20.0693	8.1067	9.8643	0.142 655
700.00	38.9675	20.1823	8.7302	10.8707	0.118 048
750.00	40.3633	20.2735	9.3538	11.8823	0.099 031
800.00	41.6742	20.3487	9.9774	12.8980	0.084 063
850.00	42.9097	20.4057	10.6010	13.9169	0.072 094
900.00	44.0776	20.4581	11.2246	14.9386	0.062 391
950.00	45.1847	20.4992	11.8482	15.9625	0.054 429
1000.00	46.2370	20.5316	12.4718	16.9882	0.047 824

^a In K. ^b In J/mol·K; eq 9. ^c In kJ/mol. ^d In kJ/mol; eq 13. ^e In kJ/mol. ^f From eqs 10 and 12.

**Figure 1.** Entropy of the electron as a function of temperature, in the three conventions.

intercept of $-0.000\ 54\ \text{J/mol}\cdot\text{K}$. At 100 K, the S_T value is only $0.042\ \text{J/mol}\cdot\text{K}$ smaller than predicted by the linear correlation. The values so obtained for S_T at certain temperatures are given in Table 1. (An expanded version of Table 1, at all integer temperatures from 1 to 1000 K, is available, as well as the data tables in units of kcal/mol or cal/mol·K, via e-mail from the author: bartmess@utkx.utk.edu.) These are shown in Figure 1, along with the values from eq 6 representing Boltzmann statistics. It is noted that solving eqs 9–11 with $k = 0$, representing Boltzmann statistics, yields the same S_T values as eq 6, to at least six significant figures. Because of the asymptotic nature of S_T as T approaches 0 K in the Boltzmann statistics, extra steps of 0.01 K were included in the numeric integration there, from 1 to 0.01 K. This was necessary to make the integrated heat capacity sum properly. This provides a check that the numerical integration method is operating correctly. At 298.15 K for the Fermi-Dirac method, $S_T = 22.7337\ \text{J/mol}\cdot\text{K}$ ($5.4335\ \text{cal/mol}\cdot\text{K}$). Although nominally the same as the value found by Mitchell of $22.7\ \text{J/mol}\cdot\text{K}$, this is fortuitous due to revisions in the values of the fundamental constants (R , N_A , m_e , k_B) and an altered standard state (1 bar as opposed to 1 atm) since the 1920s. Values at other temperatures are similarly comparable to those found by Mitchell.¹⁸

**Figure 2.** Integrated heat capacity of the electron as a function of temperature, in the three conventions.**TABLE 2: Thermochemistry of the Electron in the Three Conventions**

	EC-B ^a	IC ^b	EC-FD ^c
ΔH_f	0	0	0
ΔG_f	0	(0)	0
S_{298}	20.979	(0)	22.734 J/mol·K
$H_{298} - H_0$	6.197	0	3.146 kJ/mol
S_{0K}	$-\infty$	(0)	0
C_p	20.786		17.129 kJ/mol
E_{298}	3.720		3.720 kJ/mol

^a Electron convention, Boltzmann statistics, refs 3, 4. ^b Ion convention, refs 2, 5, 6. Parentheses denote assumed values, this work. ^c Electron convention, Fermi-Dirac statistics, this work.

The energy E_T and the heat capacity C_p are also given in Table 1. The former is from the explicit equation of Mitchell:¹⁸

$$E = \frac{3}{2} \frac{G(kT)^2 (2\pi m_e kT)^{3/2} U_{3/2}}{p^0 h^3} \quad (13)$$

and the latter is dS_T/dT , numerically obtained from the entropy data at integer temperatures.

The integrated heat capacity $H_T - H_0$ can be obtained by numerical integration of $C_p/T dT$ at the integer temperatures up to T . This is numerically equivalent to the integration of $T dS$. These values, along with the Boltzmann equivalent ones, are shown in Figure 2. At 298.15 K, the Fermi-Dirac $H_T - H_0$ equals $3.145\ \text{kJ/mol}$ ($0.7516\ \text{kcal/mol}$). To verify that the temperature step was small enough for the summation to approximate an integration, the same procedure was carried out in steps of ca. $0.25\ \text{K}$ from 1 to 300 K. The integrated heat capacity so obtained was the same to four significant figures ($3.145\ \text{kJ/mol}$) as that from one-degree steps.

The values of the thermodynamic quantities for the electron, based on the three different conventions, are summarized in Table 2. We refer to the original electron convention as "EC-B", to denote the Boltzmann statistics used, and the one developed here as the "EC-FD". As noted above, it appears that S_T from the EC-FD linearly approaches a value of 0 at 0 K, but this is not explicit in eqs 9–11.

What of the proton? This too is a fermion, and solving of eqs 9–13 for it result in the data given in Table 3. At temperatures greater than 10 K, the Boltzmann and Fermi-Dirac values differ very little, and the 298.15 K values for entropy, energy, and integrated heat capacity are essentially identical for these two methods. Unlike the electron, however, the proton is not regarded as an element, but rather a regular chemical species. We thus wish to obtain the heat of formation and similar quantities for it. The ionization energy (IE) of the hydrogen atom, as shown in reaction 3, is reported as a threshold (0 K) value. The spectroscopic value E_0 is $13.598\ 44\ \text{eV}$ ($1312.05\ \text{kJ/mol}$).^{6,8} On the basis of Scheme 1,

TABLE 3: Thermodynamics of the Proton by Fermi-Dirac Statistical Mechanics

T^a	S_T^b		C_p^c		E_T^d EC-B/FD ^f	$H_T - H_0^e$	
	EC-B	EC-FD	EC-B	EC-FD		EC-B	EC-FD
1.00	5.9648	-9.4848	2.9824	20.8055	0.0125	0.0030	0.0205
2.00	11.7572	4.9228	8.6895	21.6119	0.0249	0.0117	0.0421
5.00	25.2611	23.9696	17.3980	20.8725	0.0624	0.0576	0.1050
10.00	38.6354	38.3769	20.0954	20.8055	0.1247	0.1549	0.2091
20.00	52.8315	52.7848	20.6670	20.7908	0.2494	0.3600	0.4171
50.00	71.8358	71.8311	20.7750	20.7869	0.6236	0.9825	1.0407
100.00	86.4466	86.2390	20.7843	20.7865	1.2596	2.0424	2.0800
150.00	94.6674	94.6671	20.7855	20.7855	1.8708	3.0608	3.1194
200.00	100.6471	100.6470	20.7846	20.7859	2.4944	4.1001	4.1587
250.00	105.2854	105.2853	20.7847	20.7870	3.1179	5.1394	5.1980
273.15	107.1262	107.1261	20.7780	20.7857	3.4067	5.6206	5.6792
298.15	108.9465	108.9464	20.7847	20.7815	3.7185	6.1403	6.1988
300.00	109.0751	109.0751	20.7844	20.7868	3.7415	6.1787	6.2373
350.00	112.2793	112.2793	20.7874	20.7874	4.3651	7.2180	7.2180
400.00	115.0549	115.0549	20.7867	20.7867	4.9887	8.2573	8.2573
450.00	117.5032	117.5032	20.7840	20.7840	5.6123	9.2967	9.2967
500.00	119.6933	119.6933	20.7879	20.7879	6.2359	10.3360	10.3360

^a In K. ^b In J/mol·K, eq 9. ^c In kJ/mol. ^d In kJ/mol, eq 13. ^e In kJ/mol. ^f Exactly the same in EC-B and EC-FD.

$$\Delta H_T(\text{IE}) = E_0 + [H_T - H_0](\text{H}^+) + [H_T - H_0](\text{e}^-) - [H_T - H_0](\text{H}^*) \quad (14)$$

$$\Delta S_T(\text{IE}) = S_T(\text{H}^+) + S_T(\text{e}^-) - S_T(\text{H}^*) \quad (15)$$

$$\Delta G_T(\text{IE}) = \Delta H_T(\text{IE}) - T \Delta S_T(\text{IE}) \quad (16)$$

$$\Delta_f H_T(\text{H}^+) = \Delta H_T(\text{IE}) - \Delta_f H_T(\text{e}^-) + \Delta_f H_T(\text{H}^*) \quad (17)$$

$$\Delta_f G_T(\text{H}^+) = \Delta G_T(\text{IE}) - \Delta_f G_T(\text{e}^-) + \Delta_f G_T(\text{H}^*) \quad (18)$$

For the hydrogen atom, $S_T(\text{H}^*) = 114.713 \text{ J/mol}\cdot\text{K}$, $H_{298} - H_0 = 5/2 RT = 6.197 \text{ kJ/mol}$, $\Delta_f H_{298}^\circ = 217.965 \text{ kJ/mol}$, and $\Delta_f G_{298}^\circ = 203.246 \text{ kJ/mol}$.³ For all three conventions, the entropy of the proton is all translational: $S_T(\text{H}^+) = 108.947 \text{ J/mol}\cdot\text{K}$.²⁰ In both the EC-B and IC, $H_{298} - H_0$ for the proton is taken as that of an ideal gas, 6.197 kJ/mol.

Using these values in eqs 14–18, along with the values for the electron from Table 2, yields the data in Table 4. The enthalpy of formation for the proton in the EC-FD (1533.101 kJ/mol, or 366.42 kcal/mol) is between the values of the other two conventions. The free energy of formation of the proton in the EC-FD is smaller than those from IC and EC-B, which are comparable.¹⁰

As shown in Figure 2, the electron's integrated heat capacity by the EC-FD is always less than that by the EC-B, but by definition always greater than the zero value for the integrated heat capacity by the IC, save at 0 K. The free energies for the ionization process of hydrogen are shown in Figure 3 for the three conventions as an extension of the work of Sharpe and Richardson.¹⁰ The EC-FD coincides with the other two conventions only at 0 K. The coincidence point for the IC and the EC-B is 295.5 K, slightly different from the literature value of 297 K,¹⁰ due to the change in the standard state pressure used.

Discussion

The convention of 1 bar standard state pressure (10⁵ Pa) is used for present calculations. Although that is not an attainable pressure for a gas of like-charged ions²¹ nor even remotely "ideal",²³ it is adopted here in keeping with the conventions of thermodynamics.⁹ The discussion of the thermodynamics of the electron in the JANAF Tables³ indicates that the EC-FD integrated heat capacity approaches that of the EC-B as the standard state pressure that is used becomes much less than 1 bar. As shown in Figure 4, at even 0.01 bar the EC-FD value for $H_T - H_0$ is

TABLE 4: Thermochemistry of the Proton in the Three Conventions

	EC-B ^a	IC ^b	EC-FD ^c
$\Delta H_{298}(\text{IE})^d$	1318.249	1312.048	1315.136 kJ/mol
$\Delta S_{298}(\text{IE})^d$	15.217	-5.761	16.970 J/mol·K
$\Delta G_{298}(\text{IE})^d$	1313.713	1313.768	1310.077 kJ/mol
$\Delta_f H_{298}(\text{H}^+)$	1536.197	1529.997	1533.101 kJ/mol
$\Delta_f G_{298}(\text{H}^+)$	1516.959	1517.014	1513.324 kJ/mol

^a Electron convention, Boltzmann statistics, refs 3, 4. ^b Ion convention, refs 2, 5, 6. ^c Electron convention, Fermi-Dirac statistics, this work. ^d For reaction 3.

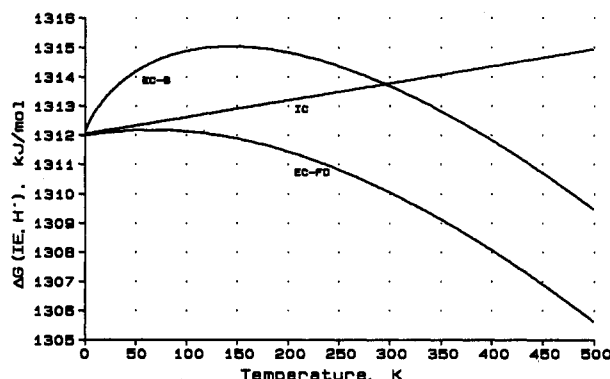


Figure 3. Free energy of ionization of the hydrogen atom as a function of temperature, in the three conventions.

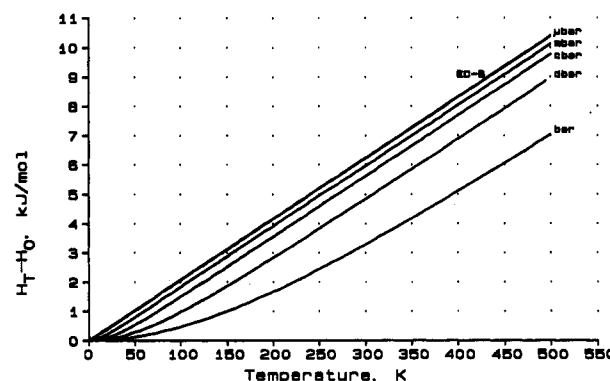


Figure 4. Integrated heat capacity of the electron as a function of temperature and standard state pressure, EC-FD versus EC-B: dbar = 0.1 bar, cbar = 0.01 bar, mbar = 0.001 bar, μbar = 0.000 001 bar.

within 0.63 kJ/mol of the EC-B values and, at 10⁻⁶ bar, is within 17 J/mol. Adopting a more achievable standard state of 10⁻⁶ bar for the electron would appear to nullify the question of a change in thermochemical values. There is a serious problem with this, however, in that it ignores the effect of such a change in standard state on the entropy: for every order of magnitude reduction in the standard state pressure, the EC-FD entropy of the electron at 298 K increases by 19.16 J/mol·K, as shown in Figure 5. For the entropy of equilibria such as reaction 7 to work out correctly, all the species must have their thermochemical values referred to the same standard state pressure. In addition, even 10⁻⁶ bar is still a millionfold higher in ion number density than most experimental techniques achieve.²³ Finally, most neutral gases do not behave exactly ideally at 1 bar, even though that is still the accepted standard state for them. Any standard state pressure is simply an arbitrary convention, to define some anchor point for those thermochemical quantities, such as entropy, that need one. The achievability of the standard state pressure is not pertinent to the values derived from experiments at high dilution.

Adoption of the EC-FD convention would alter all enthalpies and free energies of formation of both positive and negative ions, albeit by a small and constant amount. Enthalpies of formation of cations in JANAF³ or Tech Note 270⁴ would become more negative by 3.086 kJ/mol, while those of anions would become

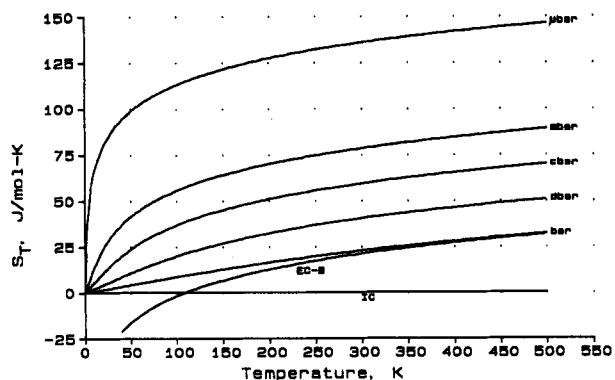


Figure 5. Entropy of the electron as a function of temperature and standard state pressure, EC-FD versus the IC and EC-B: dbar = 0.1 bar, cbar = 0.01 bar, mbar = 0.001 bar, μ bar = 0.000 001 bar.

more positive by the same amount. Cations in the GIANT Tables^{5,6} would increase in enthalpy of formation by 3.110 kJ/mol, and anions would decrease comparably. The change in convention will not affect enthalpies and free energies of reaction, other than for cases where there are unequal numbers of reactants and products (addition or fragmentation reactions). In the specific case of reaction 7, cited above as a case where the two previous conventions disagree, the EC-FD predicts an enthalpy of -2.5 kJ/mol at 400 K, consistent in direction of the temperature dependence.

For such a small change in enthalpies of formation, why both with a new convention? First, ignoring the paradigm of conventions in current thermodynamics, the EC-FD must be more correct than the EC-B or the IC. The EC-B is simply wrong; the electron does not behave that way, according to quantum mechanics.¹⁵ The IC does not represent reality; a particle with a finite rest mass should not have $H_T - H_0$ equal to zero. It must require some energy to raise the temperature of a particle. The fact that the IC is used at all may be related to the "non-rationalized" nature of current thermodynamics. Generations of students have had trouble understanding how an element can have enthalpies of formation of zero both at 0 K and at some higher temperature- T but also have $H_T - H_0$ not equal to zero; having $H_T - H_0$ equal to zero seems almost reasonable in this light.

Second, as noted for reaction 7, there are now data on experimental systems where the electron is a chemical reactant. The proper form of the thermodynamics is necessary to describe such systems; errors introduced by an arbitrary choice of convention do not cancel out.

Finally, all gas-phase ionic thermochemistry is now on computerized data bases available through NIST.⁶ It is very easy to alter these to reflect the EC-FD, and the update and distribution of such formats are far more rapid than if the data were only available in hardcopy format. This, of course, still leaves the

older data in the hardcopy literature in different conventions, but there are already two confusing conventions present in that.

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