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

\[ A + e^- \rightarrow A^- \]  (1)

and also for ionization energies

\[ M \rightarrow e^- + M^+ \]  (2)

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 \( C_V \) at 298 K 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 knowledge of the entropy \( S_T \) for the species involved.

The ionization energy of the hydrogen atom

\[ H^+ \rightarrow H^+ + e^- \]  (3)

is a special case of eq 2. This, in combination with the thermochemistry of the hydrogen atom, yields the \( \Delta H(H^+) \) and \( \Delta H(A^-) \) for the various species involved.

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 Tables7 and the NIST

**SCHEME 1**

\[
\begin{align*}
298 \text{ K} & : & \text{IP}_{298}^2 & \rightarrow \text{H}^- + \text{e}^- \\
0 \text{ K} & : & \text{IP}_0^2 & \rightarrow \text{H}^+ + \text{e}^- \\
\end{align*}
\]

Tech Note 2704. The EC declares the electron to be equivalent to an element, with both \( \Delta H \) and \( \Delta G \) therefore defined as equal to zero at all temperatures. The integrated heat capacity \( C_V \) at 0 K is taken as that for an ideal gas, \( \frac{3}{2} R \), 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 kJ/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:

\[
S_T = \frac{5}{2} R + R \ln \left\{ \frac{2 \pi m k_B T}{h^2} \right\}^{3/2} k_B G
\]

where \( h \) is Planck’s constant, \( P^0 \) is the standard state pressure, \( k_B \) is the Boltzmann constant, and \( m \) 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” compilations2 and the GIANT Tables5,6 as well as in most papers published on the subject of gas-phase ion thermochemistry. This similarly sets \( \Delta H(e^-) \) as equal to zero at all temperatures, but \( C_V \) at 0 K is also defined as equal to zero at all temperatures. The entropy and \( \Delta G \) are not clearly defined for this convention, but it seems reasonable that if the integrated heat capacity is zero, then \( C_V \) 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 compilations4,5 was 1 atm (760 Torr) but is now 1 bar (750.06 Torr) in more recent work4b,5,6 This change causes the entropy of all species, both ionic and neutral, to be greater by 0.1092 J/mol·K than previously noted.

The fundamental difference between the two conventions can be described using the thermochemical cycle in Scheme 1 for ionization energies, 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, \( \frac{3}{2} R \). \( A \) 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
temperature is assigned to the cation. In the EC, \( C = \frac{5}{3}RT \), and
the electron is taken as just another chemical species.

Sharpe and Richardson have pointed out that at a specific
327 K, the numeric value for \( \Delta G \) 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 4). This convergence of numeric values occurs because, in the EC, \( T S_p \) for the electron happens to be
numerically equal to \( HT - H_0 \) 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
thermochmistry. 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 thermochmical measurements made on gas-phase reactions with the electron as a reactant,\(^{11}\) such as

\[
\text{HI} + e^- \rightarrow 1 + H^* \tag{7}
\]

Such reactions cannot be described properly unless the thermo-
chemistry of the electron, relative to other species, is known accurately. Reaction 7 is exothermic by \(-4.2 \pm 2.0 \text{ kJ/mol} \) in the vicinity of 400 K.\(^{11}\) On the basis of what appear to be reliable data for electron affinities and bond strengths,\(^5\) the IC predicts
+3.0 \text{ kJ/mol}, while the EC predicts +3.3 \text{ kJ/mol}. Thus, determination of the proper thermochmistry 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 \( T < 109.2 \text{ K} \) 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
bosons (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, \( \alpha \) is \(-\mu/kT \) where \( \mu \) is the chemical potential, and \( \beta_i = 1/k_BT \).

\[
N_i = \frac{g_i}{e^{\beta_i e^{\beta_i}} - k} \tag{8}
\]

Examples are the electron and the proton. Bosons are indistin-
guishable particles with no constraints placed upon the occupancy on the energy levels (i.e. integral spins). These follow eq 9 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
boltszons, 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 physics and chemistry.\(^{17}\) In both the earliest\(^{15}\) 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:\(^{14}\)

\[
S = \frac{5}{2} R \frac{U_{1/2}}{U_{1/2}} - R \ln(A) \tag{9}
\]

\[
U_p = \frac{1}{\Gamma(\rho + 1)} \int \frac{u^\rho du}{1 + e^{u/k_BT}} \text{ for } \rho = 1/2 \text{ and } 3/2 \tag{10}
\]

where \( u = \epsilon/k_BT \), \( \epsilon \) is the energy of the increasing energy levels, \( A = e^{-\alpha} \), \( \alpha \) is as in eq 8, and \( k = 1 \) for Fermi–Dirac statistics. Also,\(^{18}\)

\[
pV = \frac{V GK_b(2\pi m k_b T)^{3/2} U_{3/2}}{h^3} \tag{11}
\]

The variable \( \alpha \) 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 \( \alpha \gg 1 \) (\( T < 100 \text{ K} \), eq 10 asymptotically approaches a limit and can be explicitly inte-
grated.\(^{14,18}\) For \( \alpha < 1 \) (\( T > 315 \text{ K} \), such a direct solution does not converge. Mitchell\(^{18}\) 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 \( \alpha = 1.00, 0.50, \) and 0.30). By means of a short extrapolation, a value of \( S_{398} = 22.72 \text{ J/mol} \) was obtained.

Similarly, Gordon\(^{19}\) obtained free energy values for the electron at \( T > 225 \text{ K} \), although they were not presented in an explicit \( \Delta G \) 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 \( \alpha \) out to a change in the summation of less than \( 10^{-15} \) (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 \( \alpha \), rearrangement of eq 11 gives

\[
T^{1/2} = \sqrt{\frac{P^2 h^3}{G K_b(2\pi m k_b T)^{3/2} U_{3/2}}} \tag{12}
\]

Equation 10 is evaluated as \( U_{3/2} \) for a selected value of \( \alpha \), and then a temperature corresponding to that particular \( \alpha \) is obtained from eq 12. The value of \( \alpha \) is changed iteratively in eq 10 for \( U_{3/2} \), until an \( \alpha \) is obtained that gives a temperature within 0.000 04 K of the desired integer \( T \).

For these near-integer values of \( T \) from 1 to 1000 K, the \( \alpha \) 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 \( T = 1-25 \text{ K} \) 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

<table>
<thead>
<tr>
<th>T°</th>
<th>S°b</th>
<th>C°b</th>
<th>E°d</th>
<th>H° - H°g</th>
<th>A°</th>
</tr>
</thead>
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<tr>
<td>1.00</td>
<td>0.0864</td>
<td>0.0733</td>
<td>0.0125</td>
<td>0.0000</td>
<td>0.74552E+207</td>
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<td>2.00</td>
<td>0.1724</td>
<td>0.1290</td>
<td>0.0256</td>
<td>0.0002</td>
<td>0.28457E+104</td>
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<tr>
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<td>0.4302</td>
<td>0.3872</td>
<td>0.0612</td>
<td>0.0012</td>
<td>0.25952E+42</td>
</tr>
<tr>
<td>10.00</td>
<td>0.8594</td>
<td>0.8168</td>
<td>0.1247</td>
<td>0.0043</td>
<td>0.52295E+22</td>
</tr>
<tr>
<td>20.00</td>
<td>1.7202</td>
<td>1.6806</td>
<td>0.2494</td>
<td>0.0172</td>
<td>0.21157E+11</td>
</tr>
<tr>
<td>50.00</td>
<td>4.3209</td>
<td>4.3129</td>
<td>0.6236</td>
<td>0.1083</td>
<td>1.08554E+04</td>
</tr>
<tr>
<td>100.00</td>
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<td>8.4412</td>
<td>1.2472</td>
<td>0.4322</td>
<td>7.03528E+26</td>
</tr>
<tr>
<td>150.00</td>
<td>12.7299</td>
<td>11.7097</td>
<td>1.8708</td>
<td>0.9413</td>
<td>1.11654E+49</td>
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<td>14.1470</td>
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<td>1.5921</td>
<td>1.59199E+97</td>
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<tr>
<td>250.00</td>
<td>19.8188</td>
<td>15.9126</td>
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<td>2.3469</td>
<td>1.92652E+123</td>
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<tr>
<td>273.15</td>
<td>21.2576</td>
<td>16.5561</td>
<td>3.4067</td>
<td>2.7232</td>
<td>1.47806E+176</td>
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<tr>
<td>298.15</td>
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<td>17.1373</td>
<td>3.7185</td>
<td>3.1446</td>
<td>1.14579E+216</td>
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<tr>
<td>300.00</td>
<td>22.8389</td>
<td>17.1677</td>
<td>3.7415</td>
<td>3.1764</td>
<td>1.12568E+228</td>
</tr>
<tr>
<td>350.00</td>
<td>25.5854</td>
<td>18.0575</td>
<td>4.3651</td>
<td>4.0587</td>
<td>0.72997E+274</td>
</tr>
<tr>
<td>400.00</td>
<td>28.0141</td>
<td>18.6914</td>
<td>4.9887</td>
<td>4.9786</td>
<td>0.50742E+322</td>
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<tr>
<td>450.00</td>
<td>30.2439</td>
<td>19.1478</td>
<td>5.6123</td>
<td>5.9254</td>
<td>0.37063E+370</td>
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<tr>
<td>500.00</td>
<td>32.2799</td>
<td>19.4825</td>
<td>6.2359</td>
<td>6.8917</td>
<td>0.28098E+418</td>
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<td>34.1493</td>
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<td>6.8595</td>
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<td>600.00</td>
<td>35.8749</td>
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<tr>
<td>650.00</td>
<td>37.4757</td>
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<td>8.0167</td>
<td>9.8643</td>
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</tr>
<tr>
<td>700.00</td>
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<td>20.2183</td>
<td>8.7102</td>
<td>10.8707</td>
<td>0.11804E+610</td>
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<tr>
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<td>20.2735</td>
<td>9.3538</td>
<td>11.8823</td>
<td>0.09903E+658</td>
</tr>
<tr>
<td>800.00</td>
<td>41.6742</td>
<td>20.3487</td>
<td>9.9774</td>
<td>12.8980</td>
<td>0.08406E+706</td>
</tr>
<tr>
<td>850.00</td>
<td>42.9097</td>
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<td>10.6010</td>
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<tr>
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<td>12.4718</td>
<td>16.9881</td>
<td>0.04782E+902</td>
</tr>
</tbody>
</table>

* In K. b In J/mol-K; eq 9. c In kJ/mol. d In kJ/mol; eq 13. e In kJ/mol. / From eqs 10 and 12.

TABLE 2: Thermochemistry of the Electron in the Three Conventions

<table>
<thead>
<tr>
<th></th>
<th>EC-B*</th>
<th>IC*</th>
<th>EC-FD*</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔHT</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ΔGr</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S298</td>
<td>20.979</td>
<td>(0)</td>
<td>22.734 J/mol-K</td>
</tr>
<tr>
<td>H298 - H0</td>
<td>6.197</td>
<td>0</td>
<td>3.146 kJ/mol</td>
</tr>
<tr>
<td>S298</td>
<td>-∞</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C7</td>
<td>20.786</td>
<td>0</td>
<td>17.129 kJ/mol</td>
</tr>
<tr>
<td>E298</td>
<td>3.720</td>
<td>0</td>
<td>3.720 kJ/mol</td>
</tr>
</tbody>
</table>

* Electron convention, Boltzmann statistics, refs 3, 4. 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 \( C_T \) are also given in Table 1. The former is from the explicit equation of Mitchell: \(^{18}\)

\[
E_T = \frac{3}{2} \frac{G(kT)^2(2\pi m_K T)^{3/2}}{r^2 \hbar^3}
\]  

(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 \( C_T/T \) 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 kJ/mol (0.7516 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 K from 1 to 300 K. The integrated heat capacity so obtained was the same to four significant figures (3.145 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 eV (1312.05 kJ/mol). \(^{6,8}\) On the basis of Scheme 1,
TABLE 3: Thermodynamics of the Proton by Fermi-Dirac Statistical Mechanics

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>EC-B</th>
<th>EC-FD</th>
<th>EC-B</th>
<th>EC-FD</th>
<th>EC-B/FD</th>
<th>EC-B</th>
<th>EC-FD</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>5.9648</td>
<td>-9.4848</td>
<td>2.9824</td>
<td>20.8055</td>
<td>0.0123</td>
<td>0.0030</td>
<td>0.0205</td>
</tr>
<tr>
<td>200</td>
<td>11.7572</td>
<td>4.9228</td>
<td>8.6885</td>
<td>21.6119</td>
<td>0.0249</td>
<td>0.0117</td>
<td>0.0421</td>
</tr>
<tr>
<td>500</td>
<td>52.3815</td>
<td>52.7848</td>
<td>20.6670</td>
<td>20.7908</td>
<td>0.2494</td>
<td>0.3600</td>
<td>0.4171</td>
</tr>
<tr>
<td>1000</td>
<td>71.8358</td>
<td>71.8311</td>
<td>20.7750</td>
<td>20.7869</td>
<td>0.6236</td>
<td>0.9825</td>
<td>1.0407</td>
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</table>

As shown in Figure 2, the electron's integrated heat capacity approaches that of the EC-B as the standard state pressure 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 much less than 1 bar. As shown in Figure 3 for the three conventions, the entropy of the proton is all translational: $S_T(H^+) = S_T(H^+) - S_T(H^-)$ (14)

$$\Delta S_T(IE) = S_T(H^+) - S_T(e^-) - S_T(H^-)$$ (15)

$$\Delta G_T(IE) = \Delta H_T(IE) - T \Delta S_T(IE)$$ (16)

$$\Delta H_T(H^+) = \Delta H_T(e^-) - \Delta H_T(H^-)$$ (17)

$$\Delta G_T(H^+) = \Delta G_T(e^-) - \Delta G_T(H^-)$$ (18)

For the hydrogen atom, $S_T(H^+) = 114.713 \text{ J/mol-K}$, $H_{298} - H_0 = \frac{E}{RT} = 6.197 \text{ kJ/mol}$, and $G_{298} - G_0 = 203.246 \text{ kJ/mol}$ for all three conventions, the entropy of the proton is all translational: $S_T(H^+) = 108.947 \text{ J/mol-K}$. 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) 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.

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. 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 due to the change in the standard state pressure used.

Discussion

The convention of 1 bar standard state pressure (10^5 Pa) is used for present calculations. Although that is not an attainable pressure for a gas of like-charged ions or even remotely ideal, it is adopted here in keeping with the conventions of thermodynamics. The discussion of the thermodynamics of the electron in the JANAF Tables indicates that the EC-FD integrated heat capacity approximates 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 within 0.63 kJ/mol of the EC-B value and, at 10^4 bar, is within 17 J/mol. Adopting a more achievable standard state of 10^4 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. This matter must have their thermochemical values referred to the standard state pressure, the EC-FD entropy of the electron at 298 K increases by 19.16 J/mol.

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TABLE 4: Thermochemistry of the Proton in the Three Conventions

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>EC-B</th>
<th>IC</th>
<th>EC-FD</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>52.3815</td>
<td>52.7848</td>
<td>20.6670</td>
</tr>
<tr>
<td>200</td>
<td>71.8358</td>
<td>71.8311</td>
<td>20.7750</td>
</tr>
<tr>
<td>300</td>
<td>90.2854</td>
<td>90.5745</td>
<td>20.8744</td>
</tr>
<tr>
<td>400</td>
<td>108.947</td>
<td>108.9464</td>
<td>20.9744</td>
</tr>
</tbody>
</table>

At 0 K, the EC-FD value for the proton is all translational: $S_T(H^+) = S_T(e^-) - S_T(H^-)$ (14)

$$\Delta S_T(IE) = S_T(H^+) - S_T(e^-)$$ (15)

$$\Delta G_T(IE) = \Delta H_T(IE) - T \Delta S_T(IE)$$ (16)

$$\Delta H_T(H^+) = \Delta H_T(e^-) - \Delta H_T(H^-)$$ (17)

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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 JANAF or Tech Note 2704 would become more negative by 3.086 kJ/mol, while those of anions would become...
students have had trouble understanding how an element can be in a finite rest mass should not have a finite rest mass. 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-thermalized" 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 though NIST.4 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.

Acknowledgment. This work was supported by the National Institute for Standards and Technology. We thank Dr. Sharon Lias and Dr. Alan Syverud for many helpful discussions and a reviewer for pointing out the effect on the integrated heat capacity of a much reduced standard state pressure.

References and Notes


(9) Reference 6, pp 8–12.


(20) The proton qualifies as a fermion due to the nuclear $1/2$ spin. As with the electron, this should require a value of $G = 2$ in eq 6–9. In keeping with thermochemical conventions, however, this is ignored in the calculation of the entropy, because nuclear spin is conserved in chemical reactions.

(21) A mole of like-charged ions in a cubic array of 24.4 L has a self-repulsion energy of ca. 2.9 x 10$^{12}$ kJ, or ca. 4 million atomic bombs, based on a calculated Madelung constant (Douglas, B.; McDaniel, D. H.; Alexander, J. J. Concepts and Models of Inorganic Chemistry, 2nd ed.; Wiley: New York, 1983; pp 220–223), with TNT's explosive force as 2594 kJ/kg and an atomic bomb as 25 ktons of TNT.
