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The ion and thermal electron conventions applied to free energies of ionization and electron attachment

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Abstract

Two thermochemical conventions are in common use for the electron in ionization and electron attachment processes. The thermal electron convention (TC) treats the electron as a chemical element, whereas the ion convention (IC), or stationary electron convention, treats the electron as a subatomic particle. Expressions are derived here for free energies of ionization as a function of temperature in each convention, and the differences between IC and TC values are discussed with reference to some simple systems ($H^{0/+}$, $SO_2^{0/-}$). It is found that the two conventions yield the same free energy values at about 297 K.

This paper considers the conventions related to the tabulation of free energies of formation for gas-phase ions. Compilations of gas-phase ion enthalpies and free energies of formation ($\Delta_f H$ and $\Delta_f G$ respectively) derived from spectroscopic and mass spectrometric data are available [1]. Values of $\Delta_f H$ and $\Delta_f G$ tabulated for ions depend on the convention used to treat the gas-phase electron [1(e),2]. One convention, the thermal electron convention (TC), is widely used by thermodynamicists and treats the electron as an ideal gas. The ion convention, or "stationary electron convention" (IC), is more commonly used by mass spectrometrists and treats the electron as a subatomic particle. In the JANAF tables [1(b)] free energies of formation ($\Delta_f G$) values for a small number of ions are given (in the TC), but the effect of choice of convention on the tabulated free energies and enthalpies is not explicitly discussed. In the most recent compilation of evaluated ion thermochemistry, only $\Delta_f H$(IC) values are given, and a clear discussion is presented concerning the effect of the chosen electron convention on enthalpies [1(e)]. To our knowledge an analogous discussion for $\Delta_f G$ values of ions under the two conventions has not appeared.

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A clear discussion of the two conventions for ion free energies is warranted by the increasing amount of free energy data for gas-phase ions (for negative ions see ref. 3 and for positive ions ref. 4) and the potential for inappropriate mixing of the two conventions in thermochemical cycles using these quantities. For example, if one combined ion $\Delta_f G$ values in the JANAF tables [1(b)] (TC) with ion free energies from most of the mass spectrometric literature (IC) to obtain the free energy change for a gas-phase electron transfer reaction (e.g. $A(g) + B^+(g) \rightarrow A^+(g) + B(g)$), errors would arise despite the apparent cancellation of the electrons in the final chemical equation. The estimation of ion solvation free energies is another situation in which mishandled conventions can lead to systematic errors in the derived quantities. As will be shown, in such cases free energy values derived for $T \approx 298$ K will not be much affected by the choice of electron convention, but, in general, mixing of conventions should be scrupulously avoided.

We present here a brief comparison of the two conventions for free energies of formation of ions, and illustrate the results for two simple systems. Free energies of formation for ions are traditionally obtained from spectroscopic adiabatic ionization potential (aIP) or electron affinity (EA) values combined with statistical mechanics calculations. Therefore such calculations are limited to atoms or polyatomics for which appropriate spectroscopic data are available. Recently, experimental free energies of thermal ionization and electron attachment to gas-phase polyatomic molecules have become available for an increasing number of molecules through charge-transfer equilibrium studies [3,4]. The equilibrium constants determined in these studies are of course unaffected by the choice of electron convention, but the $\Delta_f G$ (ion) values derived from the data will depend on the choice of convention.

The ionization of a gas-phase monatomic or polyatomic species M is shown in eqn. (1):

$$M(g) = M^+(g) + e^- \tag{1}$$

The free energy change for this process at a temperature T can be written in terms of the associated enthalpy and entropy changes (eqn. (2))

$$\Delta G(M \rightarrow M^+) = \Delta H(M \rightarrow M^+) - T\Delta S(M \rightarrow M^+) \tag{2}$$

Since the equilibrium in eqn. (1) cannot be studied directly, the free energy change for the process must be evaluated from other experimental data and statistical mechanics, which can provide values for the component terms in eqn. (2).

The enthalpy change for ionization ($\Delta H(M \rightarrow M^+)$) can be expressed as the sum of the enthalpy change at 0 K and the difference in heat contents of the products and reactants at temperature T, given by the difference in the integrated heat capacities over the range 0 K to T (eqn. (3)).

$$\Delta H(\mathrm{M} \rightarrow \mathrm{M}^+) = \Delta E_{0-0} + \int_0^T C_p(\mathrm{M}^+)\,\mathrm{d}T + \int_0^T C_p(\mathrm{e}^-)\,\mathrm{d}T - \int_0^T C_p(\mathrm{M})\,\mathrm{d}T \qquad (3)$$

The term ΔE_{0-0} is the energy required to form M^+ in its ground electronic, rotational and vibrational states from M in its ground state. The thermal electron convention treats the electron gas as an ideal gas, which has an integrated capacity at constant pressure of $5RT/2$, whereas under the ion convention the heat capacity of the electron is set to zero. The resulting relationship between the enthalpies of formation of the M^+ species given in the two conventions is the well-known eqn. (4):

$$\Delta_f H(\mathrm{M}^+, \mathrm{TC}) - \Delta_f H(\mathrm{M}^+, \mathrm{IC}) = 5RT/2 \qquad (4)$$

The total entropy change for the ionization process ($\Delta S(\mathrm{M} \rightarrow \mathrm{M}^+)$) is equal to $S_{\mathrm{products}} - S_{\mathrm{reactants}}$ ($= S(e^-) + S(\mathrm{M}^+) - S(\mathrm{M})$), and can be written as the sum of the translational, rotational, vibrational and electronic entropy changes (eqn. (5)):

$$\Delta S(\mathrm{M} \rightarrow \mathrm{M}^+) = \Delta S_{\mathrm{TRANS}} + \Delta S_{\mathrm{ROT}} + \Delta S_{\mathrm{VIB}} + \Delta S_{\mathrm{ELEC}} \qquad (5)$$

Since the masses of M^+ and M differ only by the mass of an electron, S_{TRANS} for M^+ and M will be virtually identical, and $\Delta S_{\mathrm{TRANS}}$ for eqn. (1) is therefore negligibly different from $S_{\mathrm{TRANS}}(\mathrm{e}^-)$. The translational entropy of an ideal gas of particles of mass m can be predicted from statistical mechanics by the Sackur–Tetrode equation * [5] (eqn. (6)) where V is the volume of the gas, k is the Boltzmann constant, N is the Avogadro constant, h is the Planck constant and T is the temperature:

$$S_{\mathrm{TRANS}} = R\left\{5/2 + \ln\left[\frac{(2\pi mkT)^{3/2}V}{Nh^3}\right]\right\} \qquad (6)$$

The term ΔS_{ELEC} is given by eqn. (7), where Q_{ELEC} is the electronic partition function (eqn. (7) assumes that no higher lying electronic states are thermally accessible). Under the ion convention only the electronic degeneracies of M and M^+ are considered, and so $\Delta S_{\mathrm{ELEC}}(\mathrm{IC})$ is never equal to zero:

$$\Delta S_{\mathrm{ELEC}} = R\ \ln[Q_{\mathrm{ELEC}}(\mathrm{products})/Q_{\mathrm{ELEC}}(\mathrm{reactants})] \qquad (7)$$

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* Although the Sackur–Tetrode equation gives good agreement between experiment and theory for atomic and molecular gases, the equation predicts negative entropies for a particle with the mass of an electron below about 89 K. These negative values are included in the curves for the thermal electron convention in Figs. 1 and 2.

The electron has an electronic degeneracy of 2, and eqn. (7) can therefore be rewritten as eqn. (8):

$$\Delta S_{\mathrm{ELEC}} = R \ln[Q_{\mathrm{ELEC}}(\mathrm{M}^+)/Q_{\mathrm{ELEC}}(\mathrm{M})] + R \ln 2 \tag{8}$$

The free energy of ionization given in eqn. (2) can now be expressed according to the two conventions. The thermal electron convention includes the terms for the electron gas, and ΔG is given by eqn. (9):

$$\begin{aligned}\Delta G(\mathrm{TC}) = \Delta E_{0-0} + \int_0^T C_p(\mathrm{M}^+)\,\mathrm{d}T - \int_0^T C_p(\mathrm{M})\,\mathrm{d}T + 5RT/2 \\ - T\{\Delta S_{\mathrm{ROT}} + \Delta S_{\mathrm{VIB}} + R \ln[Q_{\mathrm{ELEC}}(\mathrm{M}^+)/Q_{\mathrm{ELEC}}(\mathrm{M})] \\ + \mathrm{S}_{\mathrm{TRANS}}(\mathrm{e}^-) + R \ln 2\}\end{aligned} \tag{9}$$

The ion convention neglects all terms for the electron gas and ΔG of ionization is given by eqn. (10):

$$\begin{aligned}\Delta G = (\mathrm{IC}) = \Delta E_{0-0} + \int_0^T C_p(\mathrm{M}^+)\,\mathrm{d}T - \int_0^T C_p(\mathrm{M})\,\mathrm{d}T \\ - T\{\Delta S_{\mathrm{ROT}} + \Delta S_{\mathrm{VIB}} + R \ln[Q_{\mathrm{ELEC}}(\mathrm{M}^+)/\mathrm{Q}_{\mathrm{ELEC}}(\mathrm{M})]\}\end{aligned} \tag{10}$$

The resulting difference between derived $\Delta_f G(\mathrm{M}^+)$ values for each convention at any temperature is readily obtained from eqns. (6), (9) and (10) giving eqn. (11):

$$[\Delta_f G(\mathrm{M}^+, \mathrm{TC}) - \Delta_f G(\mathrm{M}^+, \mathrm{IC})]\ (\mathrm{J\ mol^{-1}}) = T[118.35 - 8.3145 \ln(T^{5/2})] \tag{11}$$

Equation (11) is derived for a standard pressure of 1 atm. At 0 K, ΔG of ionization is equal to the adiabatic ionization energy value, and the derived free energies in the two conventions are equal. In addition, eqn. (11) is also equal to zero at 296.98 K, and thus the two conventions give identical values for ΔG at this temperature. The equality of the conventions near room temperature is interesting but has no particular thermodynamic significance.

The two conventions applied to simple systems are shown graphically in Figs. 1 and 2. For M = hydrogen atom, $\Delta G(\mathrm{H} \rightarrow \mathrm{H}^+)$ values given by eqns. (9) and (10) are plotted in Fig. 1. For this system the heat capacity terms for H atom and H^+ ion essentially cancel, and ΔS_{ROT} and ΔS_{VIB} are equal to zero. The slope of the IC line is therefore determined by the value of ΔS_{ELEC}, which is $R \ln(1/2)$ (electronic excited states of the H atom can be ignored in the temperature of Fig. 1). The rapidly decreasing $\Delta G(\mathrm{H} \rightarrow \mathrm{H}^+)$ at higher temperatures under the TC is a result of an increasingly negative contribution of $T\Delta S_{\mathrm{TRANS}}(\mathrm{e}^-)$ to ΔG, which overwhelms the positive contributions of the electron heat capacity and $T\Delta S_{\mathrm{ELEC}}(\mathrm{e}^-)$. At temperatures other than approximately 297 K, the choice of convention will

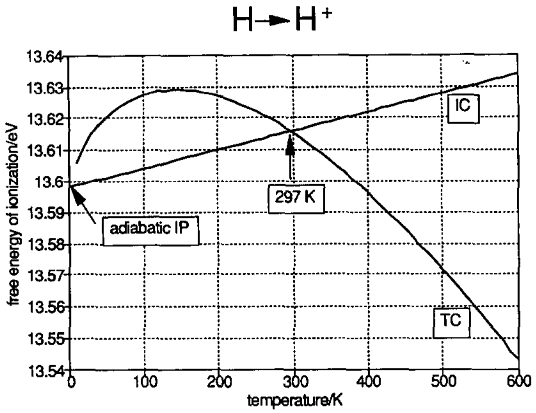

Fig. 1. Plot of the free energies of ionization calculated by using the thermal electron convention (TC) and the ion convention (IC) for atomic hydrogen.

obviously affect derived values of $\Delta_f G(H^+(g))$ and any related quantities, such as $\Delta_f G(H^+(soln))$ [6].

Free energies of ionization for polyatomic molecules can be calculated from the observed ionization potential if the energetics of the vibrational, rotational and electronic states of the neutral and ion are known. For most small molecules the $T\Delta S$ term arising from a change in electronic degeneracy will produce the largest difference between the aIP of a polyatomic molecule and ΔG of ionization under the IC at $T > 0$ K. This arises because of the relatively small changes in the contributions of vibrational and rotational degrees of freedom to the molecular partition function upon ionization of the molecule. Further, the enthalpy change arising from the

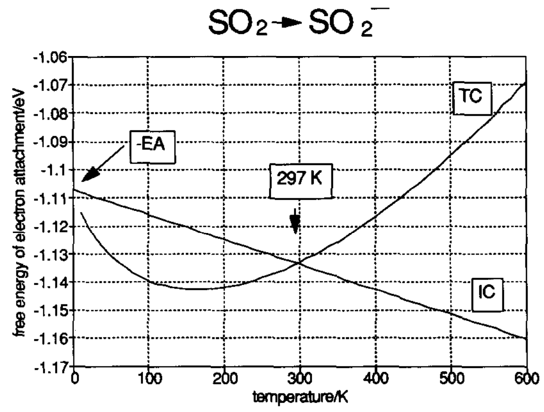

Fig. 2. Plot of the free energy of electron attachment to SO_2 calculated by using the thermal electron convention (TC) and the ion convention (IC). The negative of the electron affinity value for SO_2 is indicated.

change in the integrated heat capacities will always have the same sign as the entropy change, and these terms will cancel in the final expression.

Exactly analogous plots of ΔG for electron attachment to a neutral molecule (eqn. (12))

$$M(g) + e^- = M^-(g) \qquad (12)$$

under the two electron conventions can be obtained in the manner used to derive eqns. (9) and (10). The ΔG of electron capture for SO_2 has been calculated by Kebarle and co-workers [7] at 423 K from the electron affinity of SO_2 combined with spectroscopic and theoretical data for the geometries and vibrational frequencies of SO_2 and SO_2^-. The $SO_2^{0/-}$ couple is of particular interest since it has served as a convenient anchor for electron attachment free energy ladders determined by charge-transfer equilibrium techniques [3]. The calculation was repeated here for both electron conventions over a range of temperatures, using the same data with the exception of a new value for the electron affinity [8] (Fig. 2). In accordance with the preceding discussion, the electronic degeneracy change is dominant in the ion convention, and the dependence of ΔG(IC) on T deviates only slightly from linearity over the temperature range shown. The IC curve now shows the opposite sign of slope compared with the ionization curve of H (Fig. 1) since the open shell species (SO_2^-) appears on the right-hand side in this electron attachment process.

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