Quantum-Mechanical Calculations of Chemical Thermodynamics: Practice and Limitations

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Understanding chemical equilibrium is essential to developing a scheme to optimize the formation of desirable products in industrial reactions (Mitchell et al., 1994). Unfortunately, reliable thermodynamic data at the conditions of interest often are not available or incomplete. Experimentally, it is usually tedious to obtain the equilibrium information since the measurement must be carried out at very long residence times with a variety of compositions and temperatures in order to correlate the equilibrium over a range of conditions. It is therefore highly desirable if thermoequilibrium data could be obtained from alternative sources. There has been considerable effort recently in applying high level quantum-mechanical theory such as G2 and other ab initio methods to directly calculate thermochemistry for small molecules (Cheung et al., 1995; Trout, et al., 1996). Since high-level first principles calculations of equilibrium properties require considerable computational effort, they are usually performed only for electronic energies, which are then used to calculate the thermochemistry of specific chemical reactions (Berry et al., 1996; Hay, 1996).

In this work, we report the results of quantum-mechanical first-principles calculations of ideal gas thermodynamic properties of small organic molecules. Subsequently, the calculated heat capacity and entropy of individual molecules are used to evaluate chemical equilibrium constants for several reaction processes that are involved in the amine synthesis. The results are then compared with the results obtained from the tabulated data reported in literature (Pedley et al., 1977; DIPPR Project 801, 1991). It is generally believed that these data are reasonably reliable for small organic molecules, although some experimental evidence suggests that the reliability diminishes as the molecular size increases since the data are obtained via highly empirical methods. We show in this work that moderately high level electronic structure calculations are potentially capable of providing quantitative or semi-quantitative thermoequilibrium information for small organic systems and can be used to study chemical equilibria for reaction processes.

Our calculations utilized the adiabatic connection method, which employs a hybrid functional based on a Hartree-Fock (HF) exchange and a gradient-corrected correlation provided by density functional theory (DFT), as proposed by Becke (1993). The computational methods were made available by the PS-GVB program suite (Ringnalda et al., 1996). The calculations were performed at the 6-31G** level to maintain good accuracy. All the molecular geometries were fully optimized to obtain the minimum energy structures. We then carried out normal mode analysis to obtain the vibrational spectra. The vibrational frequencies were evaluated by computing numerical derivatives of the analytical derivatives of the energy with respect to atomic coordinates. Subsequently, partition functions of vibrational, rotational, and translational motion, from which all the thermodynamic quantities were derived, were calculated by using the standard quantum statistical model for ideal gases (Herzberg, 1966). Since we are mainly interested in chemical equilibria, we directly evaluate heats of reaction instead of heats of formation for individual molecules. Equilibrium properties can be readily derived by using the calculated heat of reaction and entropy. Comparison is then made with the tabulated values of equilibrium constants. Details of the computational procedure will be presented elsewhere (Cheng et al., 1997).

Table 1. Calculated Entropies and Zero-Point Energies

No.	Molecule	$S^0_{298°}$ (cal/mol·K) (cal.)	$S^0_{298°}$ (cal/mol·K) (tab.)	ZPE (kcal/mol)
1	CH_3OH	56.76	57.33	32.27
2	CH_3CH_2OH	64.41	67.59	50.29
3	$CH_3CH_2CH_2OH$	72.13	77.68	68.22
4	$CH_3CH_2CH_2CH_2OH$	79.74	86.86	86.15
5	NH_3	48.14	46.06	21.63
6	CH_3NH_2	57.41	58.02	40.25
7	$(CH_3)_2NH$	64.68	65.28	58.14
8	$(CH_3)_3N$	70.90	69.06	75.62
9	$CH_3CH_2NH_2$	64.78	68.13	58.32
10	$(CH_3CH_2)_2NH$	79.65	84.24	93.87
11	$(CH_3CH_2)_3N$	93.71	96.95	129.14
12	$CH_3CH_2CH_2NH_2$	71.34	77.53	75.96
13	$(CH_3CH_2CH_2)_2NH$	95.78	104.15	129.47
14	$(CH_3CH_2CH_2)_3N$	117.47	129.23	182.72
15	$CH_3CH_2CH_2CH_2NH_2$	80.11	86.82	93.99
16	$(CH_3CH_2CH_2CH_2)_2NH$	113.38	122.75	165.19
17	H_2O	45.10	45.12	13.41

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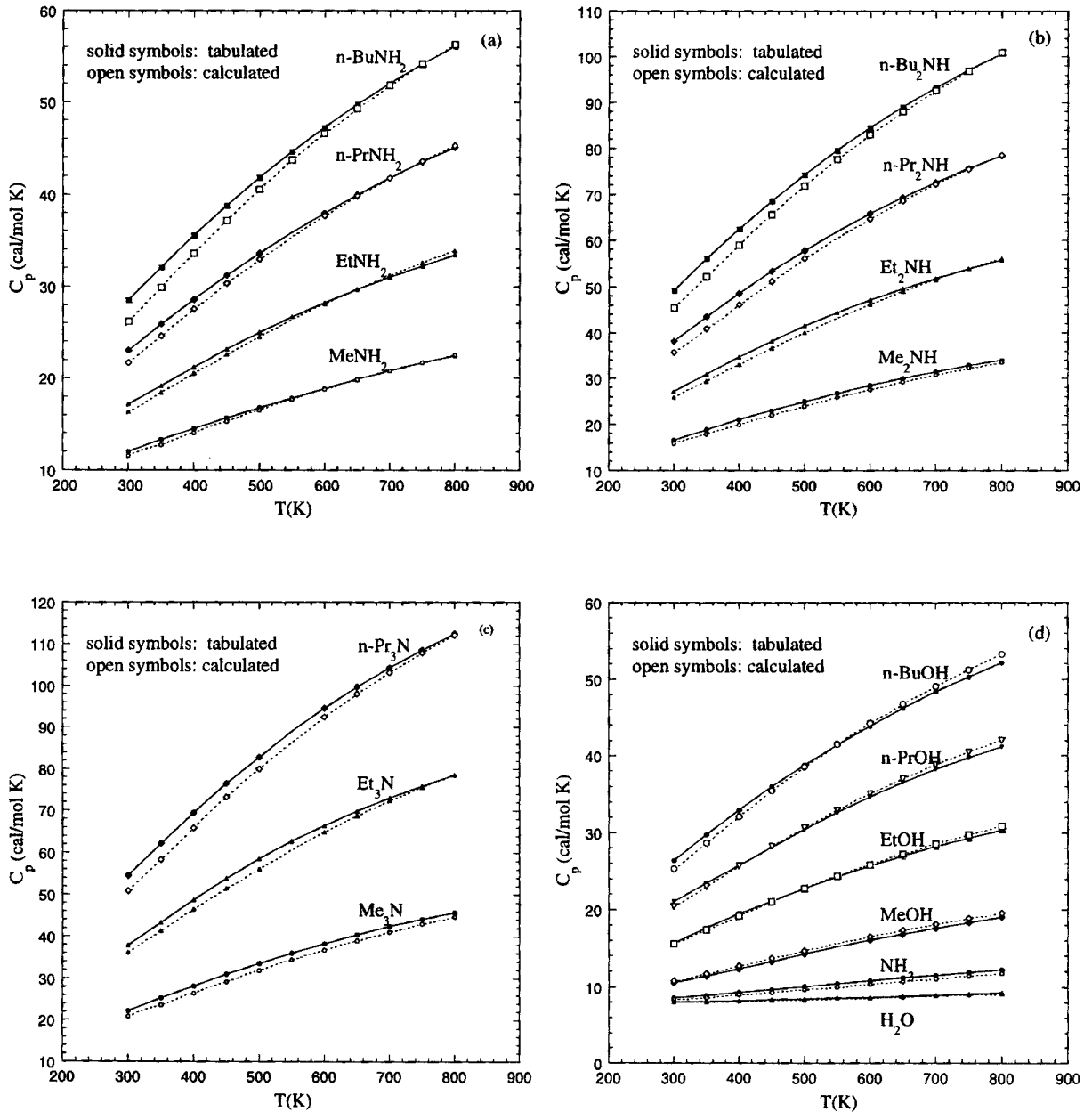

Figure 1. Calculated heat capacity vs. temperature.

The fully optimized molecular structures are carefully compared with the available geometric parameters. In general, we found that the calculated bond lengths and angles are within 0.03 Å and 2°, respectively, compared with the experimental values. Furthermore, the calculated vibrational frequencies are also in reasonable agreement with the available IR data. In this study, we are mainly interested in three fundamental quantities that determine the system equilibrium properties: heat capacity, entropy, and heat of formation. The calculated absolute entropy at room temperature for selected molecules is shown in Table 1, where, for completeness, we also present the calculated zero-point energies (ZPE). It is seen that at room temperature, the calculated entropy is in good agreement with the tabulated data. However, one indeed observes some systematic deviations from the tabulated values in the table: the larger the molecule, the larger the deviation from the tabulated entropy. This may be attributed mainly to the fact that the long chains in the large molecules, such as butylamines, give rise to a variety of conformations, which result in a certain degree of uncertainty in the low vibrational frequency modes. It is, however, the low frequency modes that contribute most significantly to the entropy. The inaccuracy of the calculated low vibrational modes is primarily responsible for the deviation from the tabulated data. The present calculation takes only the lowest energy conformation into account.

Figure 1 displays the calculated heat capacity C_p as a function of temperature at 1 atmosphere for the above molecules. It is observed that the calculated heat capacity is in excellent agreement with the tabulated values, particularly at high temperature. At lower temperature, however, there appears a certain degree of uncertainty. Once again, we also observe

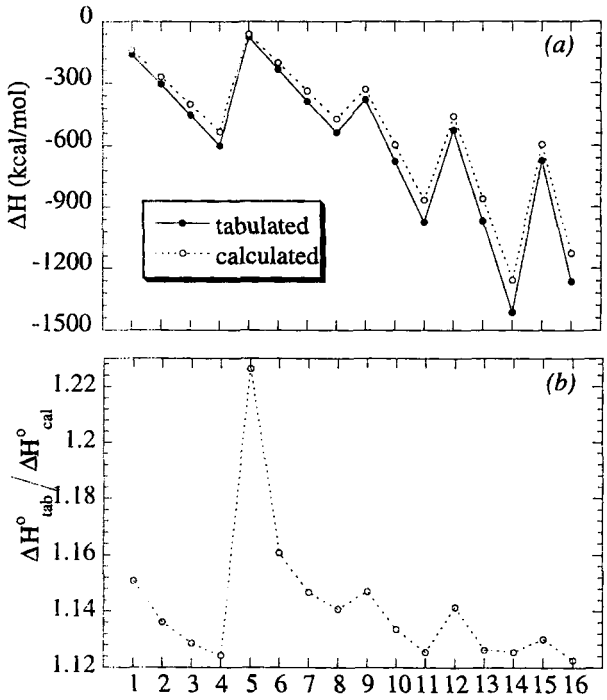

Figure 2. (a) Heats of combustion; (b) ratio of the tabulated values over the calculated values.

systematic deviation of heat capacity as molecular size increases. The largest deviation was found to be less than 4 cal/mol·K at low temperature.

We first calculate the heats of combustion for the molecules in Table 1 except for H_2O. The results are shown in Figure 2a, where the molecules are labeled with the numbers noted in Table 1. Compared with the tabulated data, we found that in general the present method systematically underestimates the heats of combustion. Detailed data analysis indicates that the ratio of the tabulated values over the calculated one decreases as the molecular size increases, as shown in Figure 2b. In particular, the ratio for NH_3 is the largest although its absolute difference of heat of combustion between the tabulated and calculated values is the smallest among the molecules. Figure 2 seems to suggest a scheme that allows scaling the calculated heats of combustion up to match the tabulated values based on the molecular sizes and specific atoms in the molecules. We will discuss the scaling scheme in detail in a future article.

The primary purpose of the present study is to use the first principles methods to calculate the equilibrium properties for chemical reaction processes of interest. As an example, we consider the industrial synthesis of methylamines (van Gysel and Musin, 1988)

$$CH_3OH + NH_3 = CH_3NH_2 + H_2O, \quad (1)$$

$$2CH_3NH_2 = (CH_3)_2NH + NH_3, \quad (2)$$

$$2(CH_3)_2NH_2 = (CH_3)_3N + CH_3NH_2. \quad (3)$$

The calculated heats of reactions and free energies at room temperature are shown in Table 2, where the tabulated data

Table 2. Heats of Reaction and Free Energies (in kcal/mol)

Reaction	$\Delta H^0_{298^\circ}$ (cal.)	$\Delta H^0_{298^\circ}$ (tab.)	$\Delta G^0_{298^\circ}$ (cal.)	$\Delta G^0_{298^\circ}$ (tab.)
$CH_3OH + NH_3 = CH_3NH_2 + H_2O$	−1.30	−4.13	−0.59	−4.06
$2CH_3NH_2 = (CH_3)_2NH + NH_3$	−3.20	−4.39	−2.61	−3.00
$2(CH_3)_2NH_2 = (CH_3)_3N + CH_3NH_2$	−2.00	−2.32	−1.71	−1.28

are also listed. The calculated values are in reasonable agreement with the tabulated ones, particularly for reactions 2 and 3. The derived equilibrium constants are shown in Figure 3. It is seen that the calculated equilibrium constants for reactions 2 and 3 are in reasonable agreement with the tabulated ones over the temperature range. However, the equilibrium constant for reaction 1 significantly deviates from the tabulated one. This is due mainly to the relatively large difference of heat of reaction between the two. In fact, detailed numerical analysis indicates that while the difference between the calculated Gibbs free energies and the tabulated ones for the molecules involved in the reactions remains almost a small constant over the entire temperature range, the error can be cumulated when the molecular free energies are used to evaluate the free energies of reactions. The small difference in molecular free energies is mainly due to the inaccuracy in the calculated heats. The difference in the heats of reaction as reflected in the Gibbs free energies is greatly magnified in the equilibrium constant, as expected.

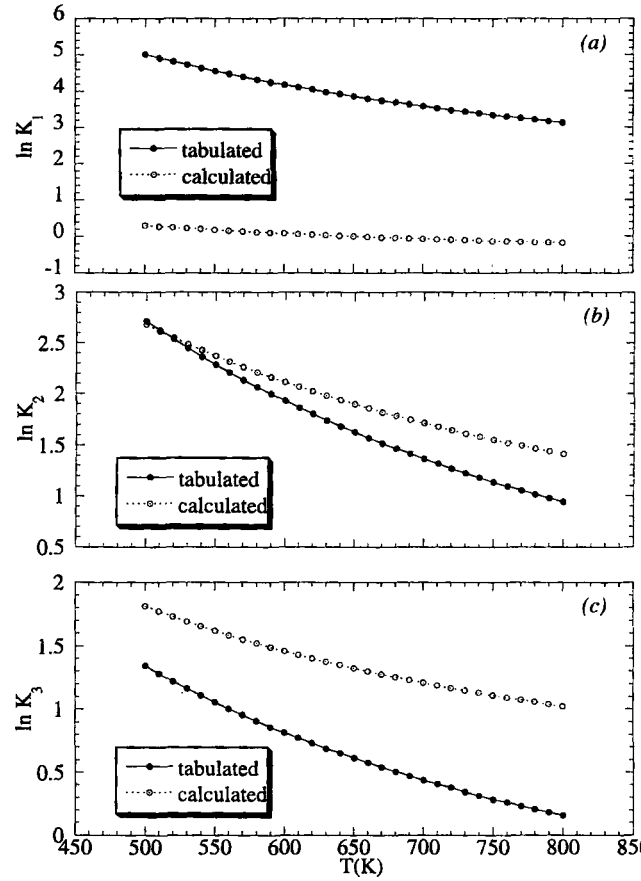

Figure 3. Equilibrium constants: (a) reaction 1; (b) reaction 2; (c) reaction 3.

In summary, we have demonstrated the potential utilities of moderately high level quantum-mechanical calculations in providing quantitative or semi-quantitative information about system equilibria for small organic molecules. We show that the hybrid HF-DFT method coupled with appropriate basis sets is particularly useful in carrying out practical calculations for systems of industrial interests due to its computational efficiency and accuracy. Our numerical results suggest that the accuracy of calculated heats of reaction will sensitively influence the calculated equilibrium constants. It is expected that the accuracy will be considerably improved upon further development of basis sets optimized for DFT calculations.

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