Study of Reaction $NH_3 + H \rightarrow NH_2 + H_2$ by a Simple Program to Determine the Reaction Rate

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We developed a simple program to determine the reaction rate by using conventional transition state theory with the Wigner transmission coefficient and also the thermodynamic properties of the species. The hydrogen abstraction in the reaction $NH_3 + H \rightarrow NH_2 + H_2$ is used as a model to demonstrate usage of the program. The rate constants have been computed for the gas-phase chemical reaction over the temperature range of 200 $K$ – 4000 $K$. To apply transition state theory, we must know the geometries, frequencies, and the potential energy for reactants and saddle point. This information is obtained from accurate electronic structure calculation performed using the GAUSSIAN98 program. Several reaction rates were calculated, each one considering the different energy calculated by the four methods and basis set. The rate constants obtained for MP4/6 – $31G**$ level both agree with experimental and theoretical results, in the temperature range, 500 – 2000 $K$.

There has been considerable interest in recent years, in the growth of boron nitride thin films. Like carbon, boron nitride has different allotropes, the most common of which are the hexagonal (hBN) and cubic (cBN) phases. The hBN, although electrically insulating, has properties that are very similar to graphite while the cBN has properties comparable to diamond.

At present there is little understanding of the chemical process which are involved in and which control the synthesis of either hexagonal or cubic boron nitride from the vapor phase. P.R.P. Barreto et al. proposed a kinetic mechanism to describe the growth of boron nitride films, for the $Ar/B/F/N/H$ system, using both CVD and arcjet reactor. The gas-phase mechanism includes 35 species and 1012 reactions and also extends a previous mechanism that contained 26 species and 67 elementary reactions. Rate constants for 117 elementary reactions were obtained from published experimental/theoretical data and those for the other 895 reactions should be estimated using transition state theory. As the number of reactions as large we developed a simple code to determine the reaction rate using conventional transition state theory with the Wigner transmission coefficient, since we normally work at high temperature, 1000 – 3000 $K$, in which the tunneling effects decreases.

To show the capability of our code we applied it to the well-known reaction $NH_3 + H \rightarrow NH_2 + H_2$, since it has been studies by several groups who provided many theoretical$^{5–10}$ and experimental results$^{11–14}$ in the temperature range of 500–2000 $K$. Comparing the results obtained using our code with the published data, our data are in a good agreement and now we can apply our code to the reaction in a $Ar/B/F/N/H$ system.

Our program has basically two subroutines, one to calculate the thermodynamic properties of the species and the other one to determine the rate constants. The input files are very easy to write down and the output files are very simple to analyze, and they can be exported, directly, to a graphical software.

The Transition State Theory (TST) was developed in the 1930s and has since formed a framework for much of the discussion of rate processes. It is a model to determine the rate constants based in an interaction potential between reactant and products with a statistical representation of the dynamics.$^{15–18}$

Considering a bimolecular reaction, such as:

\[ A + BC \rightarrow AB + C \]  

where $A$, $B$ or $C$ are atoms or group of atoms, the thermal rate constants is given by:

\[ k_{TST} = \frac{k_BT}{h} \frac{Q_{X^1}}{Q_AQ_{BC}} \exp \left(-\frac{V_{G1}}{RT}\right) \]  

where $Q_{X^1}$, $Q_A$ and $Q_{BC}$ are the partition func-

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tions of the transition state, $X^1$ (saddle point), and the reactant, $A$ and $BC$, respectively, $k_B$ Boltzmann constant, $h$ Planck constant, $T$ temperature and $R$ universal gas constant, $V^{G1}_{a}$ is the barrier:

$$V^{G1}_{a} = V^1 + \varepsilon_{ZPE}$$

where $V^1$ is the classical potential energy of the saddle point measured from the overall zero of energy and $\varepsilon_{ZPE}$ is the harmonic zero-point energy – ZPE.

We have also included the transmission coefficient, $\kappa(T)$, in equation (2):

$$k_{TST}^W = \kappa(T)k_{TST}(T)$$

where the transmission coefficient is used to account for the tunneling effect along the reaction coordinate. We have decided to estimate the transmission coefficient by using the Wigner correction \(^{15,18}\) instead of some semiclassical tunneling approximation. \(^{18}\) The Wigner correction for tunneling assumes a parabolic potential for the nuclear motion near the transition state and therefore cannot be considered as an accurate correction. The Wigner transmission coefficient is given by:

$$\kappa(T) = 1 + \frac{1}{24} \left( \frac{\hbar \omega^1}{k_B T} \right)^2$$

where the imaginary frequency at the saddle point is denoted by $\omega^1$.

For more precise rate constants calculation the variational transition state theory should be used and also semiclassical methods for the tunneling effect, \(^{18}\) yet in this case more information about the potential energy surface is required, but it is not employed in the present work. A useful way to verify the importance using the variational transition state instead of conventional transition state is the curvature of the reaction path. A constraint on reaction-path curvature is provided by the skew angle: \(^{18}\)

$$\beta = \text{ArcCos} \left( \frac{m_A m_C}{(m_A + m_B)(m_B + m_C)} \right)^{1/2}$$

where $m_A$, $m_B$ and $m_C$ are the masses of the $A$, $B$ and $C$ moieties, respectively, for the schematic reaction shown by equation (1). Large reaction-path curvature is often encountered in the tunneling region in system with small skew angles, so the tunneling effects should be smaller.

The thermodynamic properties, internal energy, entropy, and heat capacity, can be written in terms of the partition functions as: \(^{15,17}\)

$$E = k_B T \left( \frac{\partial \ln Q}{\partial \ln T} \right)_v$$

$$S = k_B \ln Q + k_B \left( \frac{\partial \ln Q}{\partial \ln T} \right)_v$$

$$c_v = k_B \left( \frac{\partial \ln Q}{\partial \ln T} \right)_v + k_B \left( \frac{\partial^2 \ln Q}{\partial (\ln T)^2} \right)_v$$

Others thermodynamic properties such as enthalpy, Gibbs free energy, can be obtained combining the previous properties.

Our code prints out the entropy, enthalpy, and heat capacity for all species, reactants, products and saddle point, as a functions of temperature.

To apply transition state theory, we must know the geometries, frequencies, and the potential energy for reactants and saddle point. These properties are obtained from accurate electronic structure calculation performed using the GAUSSIAN98 program. First, we determined the reactants and saddle point geometry and frequencies using the second order Møller-Plesset perturbation theory and the triple-zeta plus polarization 6 – 31G(d). Furthermore, we calculated the energies for all species, reactants and saddle point, at the MP2/6 – 311 + +G(3df,3pd), MP4(SDTQ)/6 – 31G ** and B3LYP/6 – 311 + +G(3df,3pd) level.

The geometries computed at MP2/6 – 31G(d) for reactant, product and saddle point are shown in table 1. These geometries are also compared with reference data. Figure 1 shows the optimized geometry of the saddle point, and also the notation used in table 1.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{reaction_system.png}
\caption{Atomic numbering of the reaction system for reaction $NH_3 + H \rightarrow NH_2 + H_2$}
\end{figure}

The harmonic vibrational frequencies calculated from \textit{ab initio} methods are overestimated, in this case, in about 8%, then we have used a scaling factor of 92%. The scaled frequencies are also compared with published data, as shown in table 2.

The first subroutine in our code calculates of the thermodynamic properties, as discussed in section 2.2. Figure 2 compares the calculated properties with the reference data from the JANAF tables \(^{20}\) for the reactants, $NH_3$ and $H$, products, $NH_2$ and $H_2$. The results are given in tables 2 and 3.
Table 1

Geometrical parameters (bond distance in Angstrons and bond angle in degree) of all stationary points of test reaction \( \text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2 \) (\(^a\) MP2/6 – 31G(d), \(^b\) HF/SSANO, \(^5\) \(\times\) MP2/6 – 31G(d), \(^6\) \(\times\) MP2/6 – 31G(d), \(^7\) J. C. Corchado et al. \(^8\) MP2/6 – 31G(d,p) \(^9\) and \(^9\) JANAF table\(^{20}\))

<table>
<thead>
<tr>
<th>Parameter</th>
<th>This work(^a)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B(^c)</td>
<td>C(^c)</td>
</tr>
<tr>
<td>(\text{NH}_3)</td>
<td>1.0168 (1.0124 (^g))</td>
<td>1.007</td>
</tr>
<tr>
<td>(R_{\text{NH}})</td>
<td>106.4004 (106.67 (^g))</td>
<td>107.4</td>
</tr>
<tr>
<td>(\text{NH}_2)</td>
<td>1.0283 (1.024 (^g))</td>
<td>1.023</td>
</tr>
<tr>
<td>(A_{\text{NH}_2})</td>
<td>103.3089 (103.4 (^g))</td>
<td>102.7</td>
</tr>
<tr>
<td>(\text{H}_2)</td>
<td>0.7375 (0.7414 (^g))</td>
<td>0.734</td>
</tr>
<tr>
<td>(T_S)</td>
<td>1.019</td>
<td>1.015</td>
</tr>
<tr>
<td>(R_{\text{NH}})</td>
<td>1.290</td>
<td>1.247</td>
</tr>
<tr>
<td>(R_{\text{NH}_2})</td>
<td>0.920</td>
<td>0.944</td>
</tr>
<tr>
<td>(A_{\text{NH}_2})</td>
<td>106.40</td>
<td>103.5</td>
</tr>
<tr>
<td>(A_{\text{NH}_2})</td>
<td>100.20</td>
<td>99.1</td>
</tr>
<tr>
<td>(A_{\text{NH}_2})</td>
<td>162.59</td>
<td>162.6</td>
</tr>
<tr>
<td>(D_{\text{NH}_2})</td>
<td>57.48</td>
<td>53.8</td>
</tr>
</tbody>
</table>

\(\text{H}_2\) and, also, gives the thermodynamic properties for the transition state \((T_S = \text{NH}_3)\).

Compared with reference data\(^{20}\) the maximum absolute errors in our calculation and the reference data are 4.71 kcal K\(^{-1}\) mol\(^{-1}\) for the \(\text{NH}_3\) entropy at 4000 K and 2.41 kcal mol\(^{-1}\) for the \(\text{NH}_3\) enthalpy at 298.15 K.

The total energies for reactants, products and saddle point as well as the reaction enthalpy and potential barrier calculated by different methods and basis set are shown in table 3, in which we applied the ZPE correction in the reaction enthalpy and potential barrier. We found a large range of values for the potential barrier, 14.39 – 25.37 kcal mol\(^{-1}\), for the methods and basis set used, as well as, for the reaction enthalpy, where this range is 0.12 – 8.68 kcal mol\(^{-1}\). The same behavior, for the potential barrier, is found in the literature, range of 7.6 – 22.6 kcal mol\(^{-1}\)\(^{5,7,9}\). We would like to emphasize the calculation made in MP4(SDTQ)/6 – 31G *, where the absolute error in the potential barrier was 0.1 kcal mol\(^{-1}\) when compared with the Garrett et al.\(^{7}\) results for the same methods and basis set.

The skew angle in this case is 46.7\(^\circ\), as it is a mid-value angle, we should expect same tunneling effects. For reactions with intermediate/high-value of the skew angle the Wigner transmission coefficient is not the best correction. On the other hand, we are interested in a high temperature range, 1000 – 3000 K, where this problem is greatly reduced.

Figure 2. Comparisons of thermodynamic properties, enthalpy and entropy, obtained by our code (symbols) with experimental data from JANAF table\(^{20}\) (lines)
The analysis of reaction
reactions we want to analyze.
and one input file describing which and how many
actants and one input file for the transition state
at once since we have one input file for all the re-
code allows us to determine several reaction rate
be used directly by some graphical software. Our
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easily. We opted to write our own code instead of
using the available ones such as POLYRATE pro-
e. Several reaction rates were calculated, each one considering the different energy calculated
by the four methods and basis set. One can see
from figure 3 that the rate constants obtained for
MP4/6–31G** level both agree with experimental
and theoretical results, in the temperature range,
500 – 2000 K.
Our purpose was to develop a simple code to de-
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The analysis of reaction \( \text{NH}_3 + H \rightarrow \text{NH}_2 + H_2 \)
allowed us to check the capability of our code. Our
code reproduce the reaction rate from the reference
data in a high temperature range, \( T > 500 \text{K} \). Now
we can extend this methodology for other reactions

### Table 2

Harmonic vibrational frequencies (\( \text{cm}^{-1} \)) and zero-point energy (\( \text{kal mol}^{-1} \)) of reaction \( \text{NH}_3 + H \rightarrow \text{NH}_2 + H_2 \)

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>( \text{NH}_3 )</td>
<td></td>
</tr>
<tr>
<td>1068 (950 (^g))</td>
<td>1146</td>
</tr>
<tr>
<td>1614(2) (1627 (^g))</td>
<td>1803(2)</td>
</tr>
<tr>
<td>3224 (3337 (^g))</td>
<td>3709</td>
</tr>
<tr>
<td>3368(2) (3444 (^g))</td>
<td>3841(2)</td>
</tr>
<tr>
<td>( \text{NH}_2 )</td>
<td></td>
</tr>
<tr>
<td>1501 (1497 (^g))</td>
<td>1516</td>
</tr>
<tr>
<td>3147 (3219 (^g))</td>
<td>3307</td>
</tr>
<tr>
<td>3259 (3301 (^g))</td>
<td>3417</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td></td>
</tr>
<tr>
<td>4170</td>
<td>4301</td>
</tr>
<tr>
<td>( \text{T}_S )</td>
<td></td>
</tr>
<tr>
<td>622</td>
<td>695</td>
</tr>
<tr>
<td>652</td>
<td>726</td>
</tr>
<tr>
<td>1033</td>
<td>1209</td>
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<td>1310</td>
<td>1408</td>
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<td>1490</td>
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<tr>
<td>3243</td>
<td>3666</td>
</tr>
<tr>
<td>3366</td>
<td>3761</td>
</tr>
<tr>
<td>2536i</td>
<td>2717i</td>
</tr>
</tbody>
</table>

Figure 3 compares the reaction rate obtained in this
work, considering conventional transition state theory
(TST) and also applying the transmission coeffi-
cient of Wigner (TST/W) with data from the ref-
erence. Several reaction rates were calculated, each one considering the different energy calculated
by the four methods and basis set. One can see
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Figure 3. Comparisons of Arrhenius plot of \( k \) against the reciprocal temperature (K) in the
range of 400 – 4000K for reactions \( \text{NH}_3 + H \rightarrow \text{NH}_2 + H_2 \) obtained in this paper with refer-
ence data where \( C, D, H, J \) and \( K \) are theoreti-
cal data from Espinosa-Garcia\(^6\), Corchado\(^5\), Mar-
shall\(^10\), Garrett\(^7\) and Espinosa-Garcia\(^9\), respec-
tively and \( E, F, G \) and \( I \) are experimental results
from Marshall\(^11\), Hack\(^14\), Michael\(^12\) and Ko\(^11\), re-
spectively.