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.[1–4] 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 **T**ransition **S**tate **T**heory (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:

$$A + BC \rightarrow AB + C \qquad (1)$$

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

$$k_{TST} = \frac{k_B T}{h} \frac{Q_{X^\ddagger}}{Q_A Q_{BC}} exp\left(-\frac{V_a^{G\ddagger}}{RT}\right) \qquad (2)$$

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

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tions of the transition state, $X^{\ddagger}$ (saddle point), and the reactant, A and BC, respectively, k_B Boltzmann constant, h Planck constant, T temperature and R universal gas constant, $V_a^{G\ddagger}$ is the barrier:

$$V_a^{G\ddagger} = V^{\ddagger} + \varepsilon_{ZPE} \qquad (3)$$

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

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

$$k_{TST}^W(T) = \kappa(T)k_{TST}(T) \qquad (4)$$

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[5, 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:

$$\kappa(T) = 1 + \frac{1}{24}\left|\frac{\hbar\omega^{\ddagger}}{k_B T}\right|^2 \qquad (5)$$

where the imaginary frequency at the saddle point is denoted by $\omega^{\ddagger}$.

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]

$$\beta = ArcCos\left[\frac{m_A m_C}{(m_A + m_B)(m_B + m_C)}\right]^{1/2} \qquad (6)$$

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]

$$E = k_B T\left(\frac{\partial \ln Q}{\partial \ln T}\right)_v \qquad (7)$$

$$S = k_B \ln Q + k_B\left(\frac{\partial \ln Q}{\partial \ln T}\right)_v \qquad (8)$$

$$c_v = k_B\left(\frac{\partial \ln Q}{\partial \ln T}\right)_v + k_B\left(\frac{\partial^2 \ln Q}{\partial(\ln T)^2}\right)_v. \qquad (9)$$

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.[19] 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.
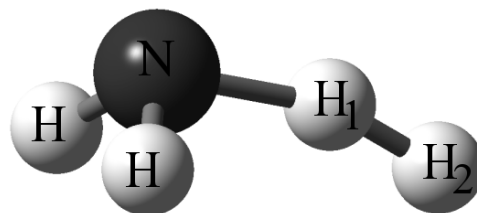

Figure 1. Atomic numbering of the reaction system for reaction $NH_3 + H \rightarrow NH_2 + H_2$

The harmonic vibrational frequencies calculated from *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

Table 1
Geometrical parameters (bond distance in Angstrons and bond angle in degree) of all stationary points of test reaction $NH_3 + H \rightarrow NH_2 + H_2$ ([a] $MP2/6-31G(d)$, [b] $HF/SSANO$,[5] [c] $MP2/6-31G(d)$,[6] [d] $MP2/6-31^*$,[7] [e] J. C. Corchado et al.,[8] [f] $MP2/6-31G(d,p)$[9] and [g] JANAF table[20])

Parameter	This work[a]	Reference				
		B[b]	C[c]	D[d]	E[e]	F[f]
NH_3						
R_{NH}	1.0168 (1.0124 [g])	1.007	1.012			1.01
A_{HNH}	106.4004 (106.67 [g])	107.4	106.1			106.1
NH_2						
R_{NH}	1.0283 (1.024 [g])		1.023			1.02
A_{HNH}	103.3089 (103.4 [g])		102.7			102.7
H_2						
R_{HH}	0.7375 (0.7414 [g])		0.734			0.73
TS						
R_{NH}	1.019	1.015	1.023	1.023	1.013	1.02
R_{NH_1}	1.290	1.247	1.305	1.305	1.286	1.30
$R_{H_1H_2}$	0.920	0.944	0.869	0.869	0.861	0.87
A_{HNH}	106.40		103.5	103.5		103.5
A_{HNH_1}	100.20	100.2	99.1	99.1		99.1
$A_{NH_1H_2}$	162.59	162.6	158.5	158.5	177.7	158.5
$D_{HNH_1H_2}$	57.48	53.8	52.7			52.7

H_2 and, also, gives the thermodynamic properties for the transition state ($TS = NH_4$).

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 NH_3 entropy at $4000 \, K$ and $2.41 \, kcal \, mol^{-1}$ for the 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 $46.7°$, as it is a midvalue 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.
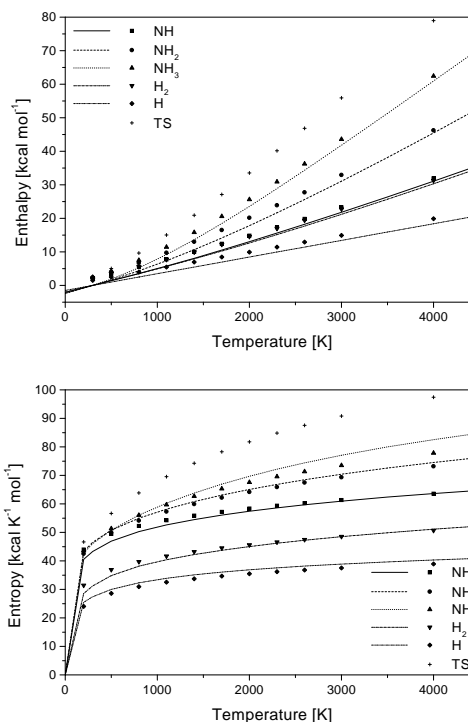

Figure 2. Comparisons of thermodynamic properties, enthapy and entropy, obtained by our code (symbols) with experimental data from JANAF table[20] (lines)

Table 2

Harmonic vibrational frequencies (cm^{-1}) and zero-point energy ($kcal\,mol^{-1}$) of reaction $NH_3+H \rightarrow NH_2+H_2$ ([a] $MP2/6-31G(d)$, [b] $HF/SSANO$,[5] [c] $MP2/6-31G(d)$,[6] [d] $MP2/6-31*$,[7] [e] J. C. Corchado et al.,[8] [f] $MP2/6-31G(d,p)$[9] and [g] JANAF table[20])

This work[a]	Reference				
	B[b]	C[c]	D[d]	E[e]	F[f]
NH_3					
1068 (950 [g])	1146	1067			1067
1614(2) (1627 [g])	1803(2)	1642(2)			1642(2)
3224 (3337 [g])	3709	3386			3386
3368(2) (3444 [g])	3841(2)	3535(2)			3535(2)
NH_2					
1501 (1497 [g])		1516			1516
3147 (3219 [g])		3307			3307
3259 (3301 [g])		3417			3417
H_2					
4170		4301			4301
TS					
622	695	683	723	563	683
652	726	694	732	598	694
1033	1209	1089	1258	1038	1089
1310	1408	1249	1485	1327	1249
1490	1633	1530	1541	1640	1530
1538	1684	1973	1731	1902	1973
3243	3666	3314	3647	3383	3314
3366	3761	3425	3750	3446	3425
2536i	2717i	1920i	2833i	1417i	1920i

Figure 3 compares the reaction rate obtained in this work, considering conventional transition state theory (TST) and also applying the transmission coefficient of Wigner (TST/W) with data from the reference.[5–14] 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 determine the reaction rate for the $B/F/H/N$ system easily. We opted to write our own code instead of using the available ones such as POLYRATE program, for example, since in that way we can simplify the inputs files and write output files that can be used directly by some graphical software. Our code allows us to determine several reaction rate at once since we have one input file for all the reactants and one input file for the transition state and one input file describing which and how many reactions we want to analyze.

The analysis of reaction $NH_3 + H \rightarrow NH_2 + H_2$ allowed us to check the capability of our code. Our code reproduce the reaction rate from the reference data in a high temperature range, $T > 500\,K$. Now we can extend this methodology for other reactions
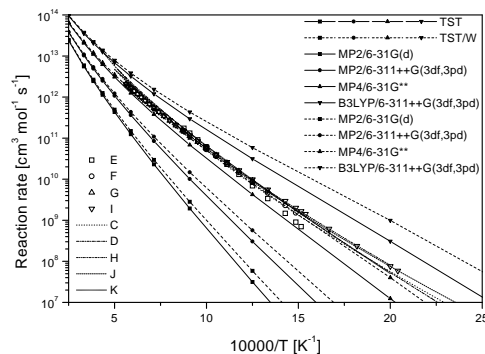

Figure 3. Comparisons of Arrhenius plot of k against the reciprocal temperature (K) in the range of $400-4000K$ for reactions $NH_3 + H \rightarrow NH_2 + H_2$ obtained in this paper with reference data where C, D, H, J and K are theoretical data from Espinosa-Garcia[6], Corchado[8], Marshall[10], Garrett[7] and Espinosa-Garcia[9], respectively and E, F, G and I are experimental results from Marshall[13], Hack[14], Michael[12] and Ko[11], respectively