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## Transition State Theory: Thermodynamics and Kinetics of Ammonia Production via DFT Functional

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## Introduction

- World War I resulted in the exploration for new synthesis methods for ammonia from gaseous nitrogen and hydrogen.

- Computational studies have indicated that a likely mechanism for the gas phase reaction has four steps:



- Within each step, there are transition state (TS) complexes. A transition state complex is an intermediate that is highly unstable, with partially formed and broken bonds. TS complexes briefly exist and are difficult to measure.

- The thermodynamics and kinetics of ammonia production are not well known and utilizing computational chemistry can help elucidate the enthalpy, entropy, and equilibrium constants for the overall reaction.

- In this investigation, we utilized density functional theory (DFT) to elucidate the energetics for the production of ammonia by PBE0 and B3LYP functionals.

- We determined which functional better describes the four-step mechanism for ammonia production and we predicted the forward and reverse rate constants for each step of the reaction from the Eyring Equation:

$$k = \frac{k_B T}{h c^\circ} e^{\frac{\Delta S^\ddagger}{R}} e^{-\frac{\Delta H^\ddagger}{RT}}, \quad (6)$$

## Method

We utilized the following settings in ChemCompute to collect the electronic energy and thermodynamic values for each molecule:

- Type: Geometry Optimization
- Add-Ons: Thermodynamics
- Basis Set: 6-31G\*
- Molecular Orbital Method: RHF
- DFT Functional: PBE0 or B3LYP
- PCM Solvent: None

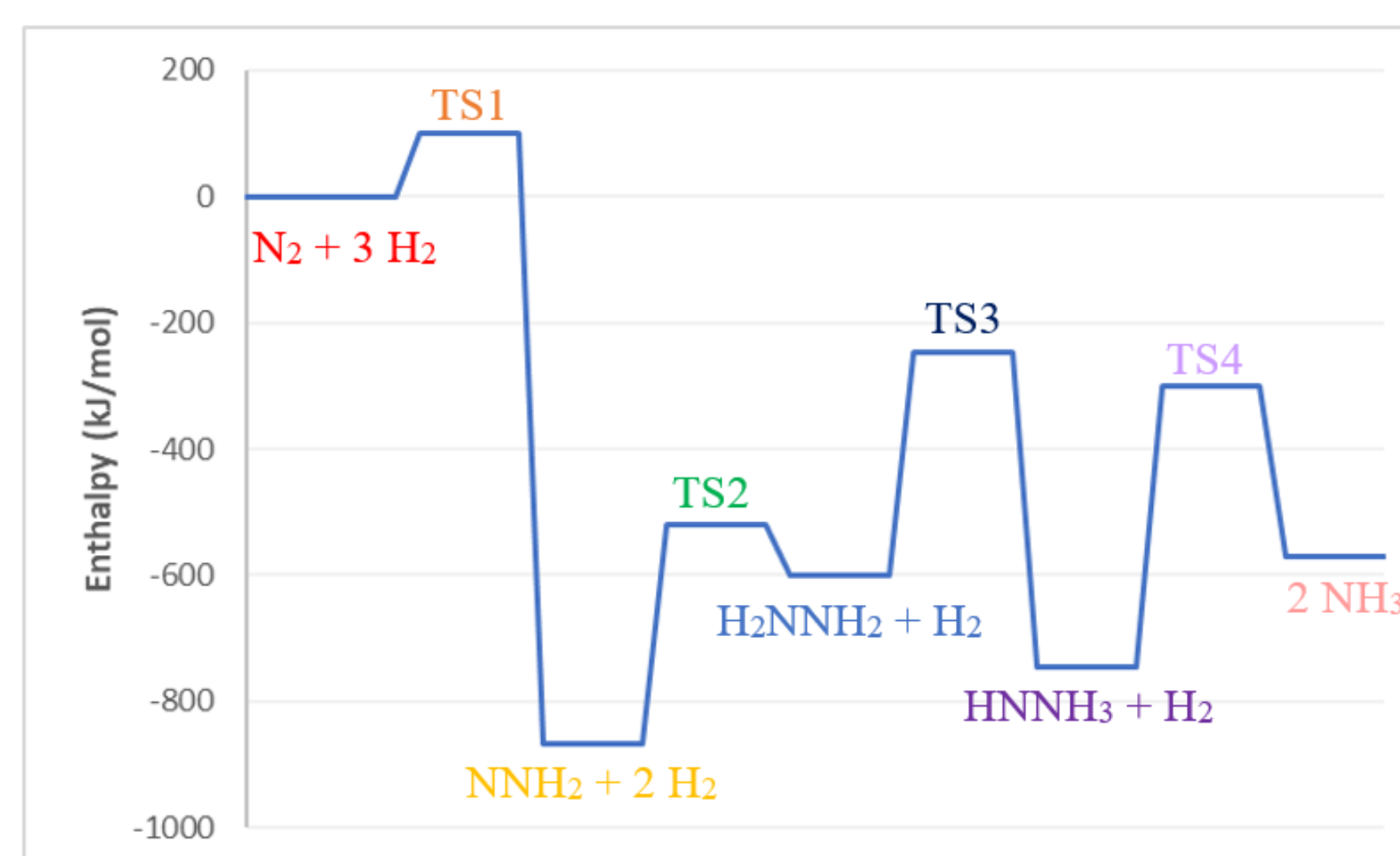
## Results

**Table 1.** Entropy and enthalpy of the overall reaction utilizing the PBE0 functional.

	Experimental	Literature <sup>2</sup>	% Error
$\Delta H_{\text{rxn}}$ (kJ/mol)	-81.32	-91.88	-11.5
$\Delta S_{\text{rxn}}$ (J/mol K)	-197.75	-198.11	-0.18

**Table 2.** Entropy and enthalpy of the overall reaction utilizing B3LYP functional.

	Experimental	Literature <sup>2</sup>	% Error
$\Delta H_{\text{rxn}}$ (kJ/mol)	-1923.02	-91.88	1990
$\Delta S_{\text{rxn}}$ (J/mol K)	-244.79	-198.11	24



**Figure 1.** Reaction coordinate diagram based on the enthalpy of each reaction stage relative to the reactants via PBE0.

**Table 3.** Forward rate constants for each transition state step utilizing PBE0.

PBE0 forward reaction				
Step	$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol K)	$\Delta n$	$k_f$
TS1	589.46	-94.71	-1	<sup>a</sup> 2.20E-75
TS2	-29.02	-114.95	-1	<sup>a</sup> 7.51E+11
TS3	243.09	14.40	0	<sup>b</sup> 8.57E-30
TS4	188.45	-95.39	-1	<sup>a</sup> 5.97E-26

<sup>a</sup> Units of M<sup>-1</sup> s<sup>-1</sup>. <sup>b</sup> Units of s<sup>-1</sup>.

**Table 4.** Reverse rate constants for each transition state step utilizing PBE0.

PBE0 reverse reaction				
Step	$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol K)	$\Delta n$	$k_r$
TS1	83.37	-0.13	0	<sup>b</sup> 2.23E-02
TS2	265.08	12.29	0	<sup>b</sup> 9.29E-34
TS3	181.83	5.60	0	<sup>b</sup> 1.63E-19
TS4	444.49	-114.21	-1	<sup>a</sup> 8.16E-72

<sup>a</sup> Units of M<sup>-1</sup> s<sup>-1</sup>. <sup>b</sup> Units of s<sup>-1</sup>.

**Table 5.** Equilibrium constants for each transition state step utilizing PBE0.

Step	TS1	TS2	TS3	TS4
$K_{\text{eq}}$	9.96E-74	1.45E+59	5.26E-11	7.31E+45

## Discussion

- PBE0 better describes the four-step mechanism for the production of ammonia due to the low percent errors and exchange correlation energy.

- B3LYP does not accurately describe the four-step mechanism because its exchange correlation energy is based upon experimental values for specific systems and geometries.

- It is proposed that the experimental values from B3LYP do not reflect the proposed geometries in the mechanism, making it less accurate.

- Therefore, a reaction coordinate diagram was drawn based on the enthalpy of each reaction stage relative to the reactants (Figure 1). The TS complexes are highly unstable and require more energy in order to briefly exist.

- The forward and reverse rate constants were determined from PBE0 data and were elucidated from Equation 6. The enthalpy, entropy, and rate constants for the forward reaction is shown in Table 3, whereas the rate constants for the reverse reaction is shown in Table 4.

- The forward and reverse rate constants were used to determine the equilibrium constant of each step by Equation 7:

$$K_{\text{eq}} = \frac{k_f}{k_r}, \quad (7)$$

- Table 5 shows the predicted equilibrium constants,  $K_{\text{eq}}$ , for each step of the proposed mechanism. Steps 1 and 3 have a relatively small  $K_{\text{eq}}$ , which signifies that these steps favor the reactants. In contrast, steps 2 and 4 have a relatively large  $K_{\text{eq}}$ , signifying that the products are favored.

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## References

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