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Using Transition State Theory to Understand the Kinetics for the Gas-Phase Synthesis of Ammonia

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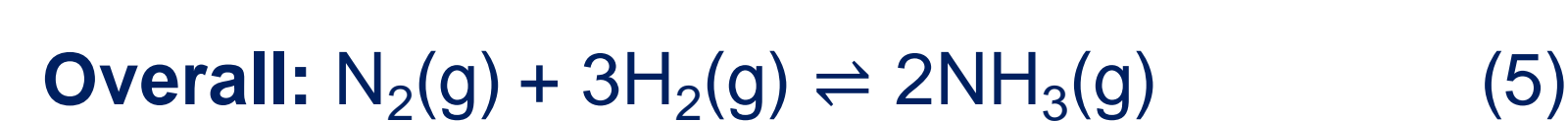
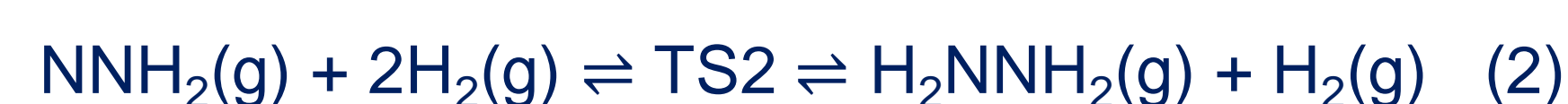
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Introduction

Haber-Bosch Synthesis

- Primary industrial method for synthesizing gas-phase ammonia
 - Ammonia used in fertilizers to restore nitrogen content back into the soil (1)
- Theoretically, a fast and spontaneous reaction because overall reaction change in Gibbs free energy (ΔG_{rxn}) and enthalpy (ΔH_{rxn}) are negative; however, the reaction rate is very slow and is typically catalyzed using an iron catalyst
- Proposed reaction mechanism:



- Finding the rate-determining step using transition state theory allows for the creation of more effective catalysts (2)

Transition State Theory

- States that an unstable high-energy activated complex exists in equilibrium with the reactants and will either revert into the reactants or decay into the product (3)
 - Rate-determining step has the largest change in energy between the reactants and the transition state
- Definition of Eyring theory, the formulaic representation of this assumption:

$$k = \frac{k_b T}{h c^*} e^{\Delta S_c/R} e^{-\Delta H_c/RT} \quad (5)$$

where k_f or k_r is the forward or reverse rate constant in $M^{-1}s^{-1}$, k_b is the Boltzmann constant, 1.380×10^{-23} J/K, T is 298.15 K, h is Planck's constant, 6.626×10^{-34} J*s, c^* is the standard state concentration, 1 M, ΔS_c is the change activated complex entropy in J/mol*K, R is the gas constant 8.314 J/mol*K, and ΔH_c is in J/mol (3).

- Using k_f and k_r to find K_{eq} for each step using the relationship (2,5),

$$K_{eq} = k_f / k_r \quad (6)$$

- If $K_{eq} \gg 1$, forward reaction is favored
- If $K_{eq} \ll 1$, reverse reaction is favored

- K_{eq} shows the thermodynamic favorability for each step

Goals

- Obtain electronic energies of the reactants, intermediates, and transition states using the computational chemistry program GAMESS and the basis sets 6-31G*, 6-311G**, and STO-3G (4)
 - Results and Equations 5 and 6 used to find k_f 's, k_r 's, and K_{eq} 's for each step to see thermodynamic favorability
- Creation of reaction coordinate diagram using the measured enthalpies for the reactants, intermediates, and transition states to identify the rate-determining step
- Comparison of experimental ΔG_{rxn} 's, ΔH_{rxn} 's, and ΔS_{rxn} 's to literature to determine the best basis set

Experimental

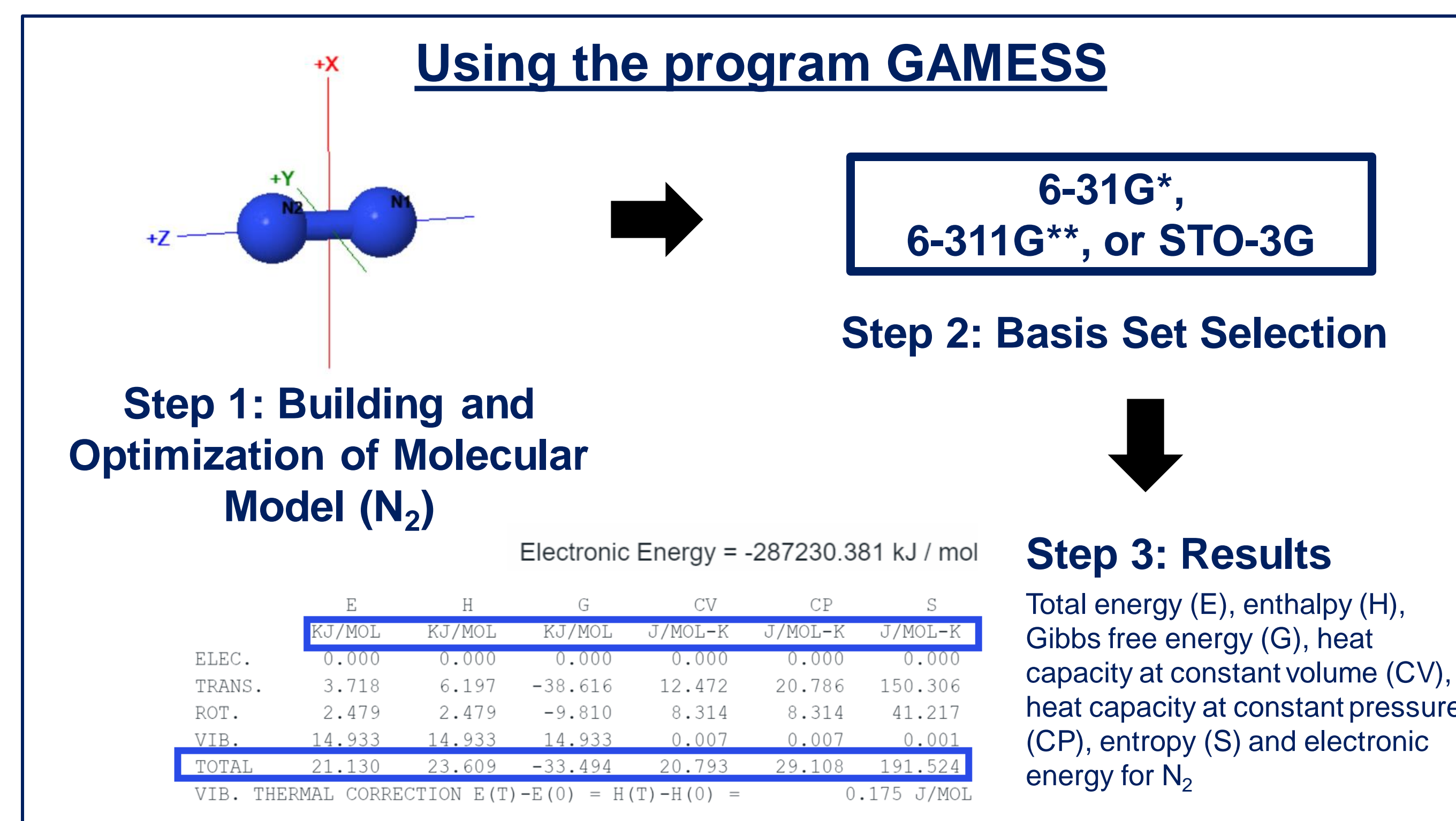


Figure 1: Procedure for obtaining molecular electronic energies using GAMESS. Transition state models were generated from provided coordinates (2)

Results

Table 1: Average k_f 's, k_r 's, K_{eq} 's and ΔG_{rxn} for each synthesis step

	N ₂ (g) + 3H ₂ (g) \rightleftharpoons TS1 \rightleftharpoons NNH ₂ (g) + 2H ₂ (g)			
	Average k_f (M ⁻¹ s ⁻¹)	Average k_r (M ⁻¹ s ⁻¹)	K_{eq}	ΔG_{rxn} (J/mol)
Basis Set: 6-31G*	6.8508E-27	1.6230E+09	4.2085E-36	2.0191E+05
Basis Set: 6-311G**	1.2347E-26	2.9544E+09	4.1792E-36	2.0193E+05
Basis Set: STO-3G	1.4131E+13	3.4217E+44	4.1297E-32	1.7913E+05
	NNH ₂ (g) + 2H ₂ (g) \rightleftharpoons TS2 \rightleftharpoons H ₂ NNH ₂ (g) + H ₂ (g)			
Basis Set: 6-31G*	1.6203E+27	3.0250E+09	5.3818E+18	-1.0691E+05
Basis Set: 6-311G**	6.6463E+27	1.9325E+06	3.4392E+21	-1.2292E+05
Basis Set: STO-3G	-	1.2441E+13	-	-
	H ₂ NNH ₂ (g) + H ₂ (g) \rightleftharpoons TS3 \rightleftharpoons HNNH ₃ (g) + H ₂ (g)			
Basis Set: 6-31G*	1.3320E-19	6.2912E+12	2.1190E-32	1.8078E+05
Basis Set: 6-311G**	2.2412E-22	6.2178E+12	3.6044E-35	1.9659E+05
Basis Set: STO-3G	3.2144E-38	6.2464E+12	5.1486E-51	2.8703E+05
	HNNH ₃ (g) + H ₂ (g) \rightleftharpoons TS4 \rightleftharpoons 2NH ₃ (g)			
Basis Set: 6-31G*	1.5562E+10	6.7022E-54	2.3219E+63	-3.6167E+05
Basis Set: 6-311G**	3.3021E+10	3.3927E-56	9.8392E+65	-3.7667E+05
Basis Set: STO-3G	2.1548E+25	5.1721E-54	4.2248E+78	-4.4877E+05

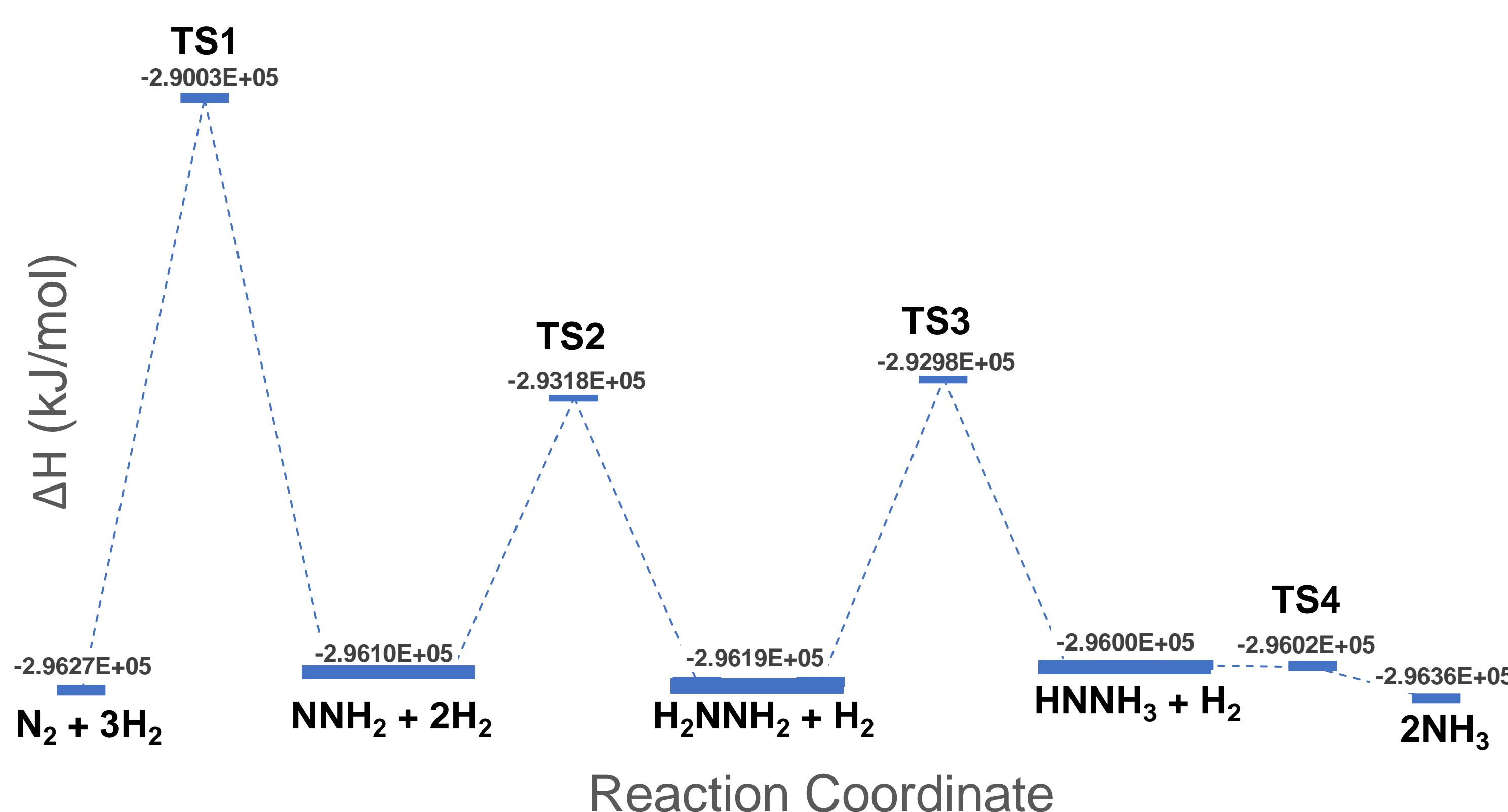


Figure 2: Reaction coordinate diagram for the ammonia synthesis based on the measured enthalpies of the transition states and the forward and reverse ΔH 's of the reactants obtained using 6-31G*

Table 2: Literature and experimental ΔH°_{rxn} 's, ΔS°_{rxn} 's, and ΔG°_{rxn} 's for each basis set

		Overall Reaction: N ₂ (g) + 3H ₂ (g) \rightleftharpoons 2NH ₃ (g)		
	Literature	ΔH°_{rxn} (J/mol)	ΔS°_{rxn} (J/mol*K)	ΔG°_{rxn} (J/mol)
Basis Set: 6-31G*	Experimental	-9.1800E+04	-1.9810E+02	-3.2736E+04
Basis Set: 6-311G**	Experimental	-9.6639E+04	-6.7433E+01	-7.6534E+04
Basis Set: STO-3G	Experimental	-1.2118E+05	-6.7463E+01	-1.0107E+05
Basis Set: 6-31G*	Error (%)	-4.4273E+04	-1.9615E+02	1.4209E+04
Basis Set: 6-31G*	Error (%)	5.2712E+00	-6.5960E+01	1.3379E+02
Basis Set: STO-3G	Error (%)	-5.1772E+01	-9.8536E+01	-1.4340E+02
Basis Set: 6-311G**	Error (%)	3.2005E+01	-6.5945E+01	2.0873E+02

Discussion

Step 1 Was Rate-Determining

In Table 1, the basis set 6-31G* revealed Step 1 had the smallest K_{eq} of 4.2085×10^{-36} . Because its K_{eq} was significantly smaller than 1, the equilibrium favored the reactants. The reaction coordinate diagram in Figure 2 revealed that TS1 had the greatest distance between reactant and transition state enthalpy (ΔH_c) of 195.123 kJ/mol; therefore, Step 1 was the rate-determining step because this step required the most energy in order to proceed (3,6).

TS4 Was the Most Stable Transition State

The reaction coordinate diagram in Figure 2 showed the most stable transition state was TS4 from Step 4 which had the smallest ΔH_c of -17.058 kJ/mol.

Basis Set 6-31G* Was the Most Accurate

Table 2 revealed that 6-31G* was the most accurate basis set with the lowest error for its ΔG_{rxn} 's, ΔH_{rxn} 's, and ΔS_{rxn} 's.

Though STO-3G had lower errors for ΔS_{rxn} and ΔG_{rxn} compared to 6-311G**'s errors, it had enthalpies for the forward and reverse equilibrium reactions that were so large that k_f for Step 2 could not be calculated. STO-3G assumes that all orbitals are spherical and cannot describe electron distribution between bonds like 6-31G* and 6-311G* (7).

Conclusion

- 6-31G* was the most accurate basis set and STO-3G could not be used because it assumes electron distribution is unaffected by environment
- Step 1 was the rate determining step because it needed the most energy to form its transition state and be converted into the products

Future Work

- Finding the kinetics, thermodynamics, and transition state energies of the catalyzed ammonia synthesis and comparing the results to the uncatalyzed synthesis
- Comparing the basis set 6-311G**+ to 6-31G*

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