



## **Ab initio Quantum chemical Calculations of high Temperature Gas Phase Equilibrium Constants**

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The thermochemistry of high temperature organic gases has direct application to the understanding of volcanic systems (Chiodini & Marini, 1998) and prebiotic organic synthesis (Miyakawa *et al.*, 2002). For instance, volcanic gases such as carbon monoxide (CO) and carbonyl sulfide (COS) are implicated in the formation of primordial carboxylic acids and peptides (Leman *et al.*, 2005), thus steering prebiotic chemistry toward protein generation. A predictive capability for high PT organic gas phase equilibria is critical. Especially noteworthy here are Pople's G-*n* (Curtiss *et al.*, 1998) and Petersson's CBS-*x* (Ochterski *et al.*, 1996) high accuracy model chemistries.

High temperature gas phase equilibria have been the focus of several *ab initio* studies, however, serious disagreements remain between experimental measurement and theoretical calculation of reaction energies. For instance, reported experimental and calculated *ab initio* (Bohr & Henon, 1998) reaction energies for the Haber process ( $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$ ) in the temperature range 298.15 through 600K vary from 1.2kcal to approximately 2kcal/mol, respectively.

In this report, we present results for gas phase equilibria for a series of reactions including CO,  $\text{C}_n\text{H}_{2n}$ ,  $\text{C}_n\text{H}_{2n+2}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{H}_2\text{CO}$ , COS,  $\text{CS}_2$ ,  $\text{NH}_3$ , HCN, HCNO synthesis from starting  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{H}_2$  from 298.15K to 1500K using high accuracy quantum chemical methods (G2, G3, CBS-QCI/APNO). We briefly introduce the procedure by which thermochemical properties for gas phase reactions are calculated, followed by an assessment of available experimental high temperature gas equilibria data, against which the quality of *ab initio* computation methods is evaluated. Finally, we discuss the potential of *ab initio* thermochemistry for predicting gas phase organic synthesis equilibria in select high temperature environments.