

## Example: thermodynamics

The development of a computational scheme that can accurately predict reaction energies requires some care. As shown in Table 1 energy errors associated with ab initio calculations can be quite high. Even though ab initio electronic structure methods are constantly being developed and improved upon, these methods are rarely able to give heat of formations of a broad class of molecules with error limits of less than a few kcal/mol. Only when very large basis sets such as the correlation-consistent basis sets, high level treatments of correlation energy such as coupled cluster methods (CCSD(T)), and small correction factors such as core-valence correlation energies and relativistic effects, are included will the heat of formation from ab initio electronic structure methods be accurate to within one kcal/mol. Although one can now accurately calculate the heats of formation of molecules with up to 6 first row atoms, such high-level calculations are extremely demanding and scale computationally as  $N^7$  for  $N$  basis functions.

Table 1: Average error in calculating atomization energies with various ab initio methods.

Method	Energy Errors	Formal Scaling
HF	60 kcal/mole	$N^4$
MP2	5 kcal/mole	$N^5$
CCSD(T)	1 kcal/mole	$N^7$
DFT(LSDA)	90 kcal/mole	$N^3$
DFT(B3LYP)	3 kcal/mole	$N^4$
DFT(GGA)	20 kcal/mole	$N^3$

Examples of these types of large errors are shown in Table 2. Enthalpies of formation of  $\text{CCl}_3\text{SH}$  are calculated by using atomization energies from different levels of ab initio theory. Differences of up to 110 kcal/mol are found between different levels of ab initio theories. This example demonstrates that care must be taken in choosing the appropriate method for calculating heats of formation from total atomization energies.

**TABLE 2:** Ab initio values of standard enthalpy of formation ( $\Delta H_f^\circ(298\text{K})$ ) for  $\text{CCl}_3\text{SH}$  species calculated using the ab initio determined atomization energies.

	MP2/ cc-pVDZ	LDA/ DZVP2	BP91/ DZVP2	B3LYP/ DZVP2	G2 Theory
$\Delta H_f^\circ$	4.86	-79.99	-2.58	26.50	-12.95
All quantities are in kcal/mol.					
Results taken from E.J. Bylaska, D.A. Dixon, and A.R. Felmy(2000), "The Free Energies of Reactions of Chlorinated Methanes with Aqueous Monovalent Anions: Application of ab initio Electronic Structure Theory", J. Phys. Chem. A, <b>104</b> (3), 610-617.					

Difficulties associated with calculating absolute heats of formation from atomization energies can be avoided by using a set of isodesmic reactions (see Hehre, W. J., L. Radom, P.v.R. Schleyer, and J.A. Pople *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986). The defining property of an isodesmic reaction - that there are an equal number of like bonds on the left-hand and right-hand sides of the reaction - helps to minimize the error in the reaction energy. These reactions are designed to separate out the interactions between molecular substituents and non-bonding electrons from the direct bonding interactions by having the direct bonding interactions largely cancel one another. This separation is quite attractive. Most ab initio methods give substantial errors when estimating direct bonding interactions due to the computational difficulties associated with electron pair correlation, whereas ab initio methods are expected to be more accurate for estimating neighboring interactions and long-range through-bond effects.

The following isodesmic reaction can be used to determine the enthalpy of formation for CCl<sub>3</sub>SH that is significantly more accurate than the estimates shown in Table 2.



The first step is to calculate the reaction enthalpy of this reaction from electronic, thermal and vibrational energy differences at 298.15K at a consistent level of theory. The defining property of an isodesmic reaction that there are an equal number of like bonds on the left-hand and right-hand sides of the reaction helps to minimize the error in the calculation of the reaction energy. The enthalpy of formation of CCl<sub>3</sub>SH can then be calculated by using Hess's law with the calculated enthalpy change and the experimentally known heats of formation of the other 3 species (see Table 4).

$$\Delta H_f \text{CCl}_3\text{SH} = \Delta H_f \text{CH}_3\text{SH}(\text{exp}) + \Delta H_f \text{CCl}_3\text{H}(\text{exp}) - \Delta H_f \text{CH}_4(\text{exp}) - \Delta H_f(\text{calc}).$$

Results of calculations for enthalpies of formation using this isodesmic strategy are shown in Table 3. This computationally tractable strategy significantly reduces energetic errors and is able to provide accurate heats of formation, within a few kcal/mol.

**TABLE 3:** Gas-phase standard enthalpies of formation ( $\Delta H_f^\circ(298\text{K})$ ) from isodesmic reactions and G2 Theory calculations.

	$\Delta H_f^\circ(298.15\text{K})$				$\Delta H_f^\circ(298.15\text{K})$	
	(isodesmic formulation)				G2	Expt.
	MP2/ cc-pVDZ	LDA/ DZVP2	BP91/ DZVP2	B3LYP/ DZVP2		
<b>CCl<sub>3</sub>SH</b>	-13.40	-11.86	-8.68	-7.64	-12.95	
<b>CHCl<sub>2</sub>SH</b>	-11.48	-11.07	-8.66	-7.92	-11.52	
<b>CH<sub>2</sub>CISH</b>	-7.01	-6.66	-5.44	-5.20	-6.98	
<b>CH<sub>3</sub>SH</b>					-4.76	-5.34

All quantities are in kcal/mol. The isodesmic exchange reactions are:  $\text{CCl}_x\text{H}_y\text{N} + \text{CH}_4 \rightarrow \text{Cl}_x\text{H}_{y+1} + \text{CH}_3\text{N}$ .

Results taken from E.J. Bylaska, D.A. Dixon, and A.R. Felmy(2000), "The Free Energies of Reactions of Chlorinated Methanes with Aqueous Monovalent Anions: Application of ab initio Electronic Structure Theory", *J. Phys. Chem. A*, **104**(3), 610-617.

**TABLE 4:** Miscellaneous experimental gas-phase enthalpies of formation (kcal/mol).

Compounds	$\Delta H_f^\circ$
<b>H</b>	52.095
<b>C</b>	171.291
<b>S</b>	66.636
<b>Cl</b>	29.082
<b>CCl<sub>4</sub></b>	-24.59
<b>CCl<sub>3</sub>H</b>	-24.65
<b>CCl<sub>2</sub>H<sub>2</sub></b>	-22.10
<b>CClH<sub>3</sub></b>	-19.32
<b>CH<sub>4</sub></b>	-17.88
<b>CH<sub>3</sub>SH</b>	-5.34

Data from Chase, M. W., Jr. *Phys. Chem. Ref. Data, Monograph No. 9* **1998**, 9, 1-1951.

## Suggested Calculations:

In this session, we are asking you to design and run NWChem simulations that can be used to estimate the enthalpy of formation for  $\text{CCl}_3\text{SH}$ . Estimate  $\Delta H_f^\circ(\text{CCl}_3\text{H})$  using its atomization energy and using the reaction enthalpy of the isodesmic reaction



*Try designing simulations that use the SCF, DFT, and NWPW modules.*

Geometries for  $\text{CCl}_3\text{SH}$ ,  $\text{CH}_3\text{SH}$ ,  $\text{CCl}_3\text{H}$  and  $\text{CH}_4$  which are needed to design your simulations can be generated using ECCE's ebuilder program (or alternatively can be obtained from the file thermodynamics.xyz). You will also need to calculate the energies for the H, C, S, and Cl atoms. The multiplicities for these atoms are 2, 3, 3 and 2 respectively.

You will also need to calculate the enthalpy of a molecule. The enthalpy of a molecule at 298.15K is sum of the total energy and a thermal correction to the enthalpy. A good estimate for the thermal correction to the enthalpy can be obtained from a frequency calculation.

$$H = E + H_{\text{correction}}$$

Temperature	=	298.15K		
Zero-Point correction to Energy	=	1.067 kcal/mol	(	0.001701 au)
Thermal correction to Energy	=	2.607 kcal/mol	(	0.004155 au)
Thermal correction to Enthalpy	=	3.200 kcal/mol	(	0.005099 au)
Total Entropy	=	52.225 cal/mol-K		
- Translational	=	38.368 cal/mol-K	(mol. weight =	63.9441)
- Rotational	=	13.602 cal/mol-K	(symmetry # =	2)
- Vibrational	=	0.255 cal/mol-K		

Thermodynamic output  
from a frequency  
calculation