# Thermochemistry with Quantum Mechanics

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## Introduction

In this practical, the heat of combustion of propane and naphthalene will be calculated using Hartee-Fock and Density functional theory technique.

The Hartree-Fock method approximates the ground-state wavefunction and ground-state energy of many-body systems.

Density Functional Theory treats fields of properties of a system as functionals dependant on the electron density of the system.

First, using Hartree-Fock and DFT respectively, the enthalpy of formation of products and reactants in the combustion of both propane and naphthalene will be calculated. Then the net difference between the standard enthalpy of formation between products and reactants will be calculated. This value will be of $∆H$ will be equal to the heat energy evolved in the combustion of the molecule in oxygen.

Take the empirical equation for the combustion of propane:

$$x\left(C\_{3}H\_{8}\right)+y\left(O\_{2}\right)\rightarrow z\left(CO\_{2}\right)+q(H\_{2}0)$$

where x, y, z and q are arbitrary values for the number of each constituent. The change in enthalpy for the reaction (and hence the heat of combustion) is given by the equation:

$$ ∆H=zE\_{CO\_{2}}+qE\_{H\_{2}0}-xE\_{C\_{3}H\_{8}}-yE\_{O\_{2}}$$

Where EX is the enthalpy of formation of a constituent x.

Similar calculation will be carried out for naphthalene.

The values obtained for the heat of combustion will be compared to given experimental values and any discrepancy will be evaluated.

### Question 1:

The balanced equation for the combustion of propane:

$$\left(C\_{3}H\_{8}\right)+5\left(O\_{2}\right)\rightarrow 4\left(CO\_{2}\right)+3(H\_{2}0)$$

Computations carried out were for molecules at 0K, and hence ignored the thermal energy of molecules. The values recorded included thermal correction for combustion at 298K. The respective estimated enthalpies of combustion of products and reacted are tabulated below in units of kJ/mol.

|  |  |  |
| --- | --- | --- |
|  | DFT | HF |
|  | -312540 | -310202.864 |
| o2 | -394669 | -392814.566 |
| co2 | -495107 | -492605.404 |
| h20 | -200585 | -199516.907 |

 The energy released in the combustion of one mole if propane was estimated according to the equation:

$$ ∆H=3E\_{CO\_{2}}+4E\_{H\_{2}0}-E\_{C\_{3}H\_{8}}-5E\_{O\_{2}}$$

The value obtained for $ ∆H$ for the combustion of propane using Density functional Theory values was 1773.63kJ/mol. Using values obtained via Hartree-Fock, $∆H$ was calculated to be 1608.14kJ/mol.

### Question 2

The experimentally determined value for the enthalpy of combustion of propane at 298K is 2222.0 kJ/mol. The value obtained via DFT was short of this value. The

### Question 3

The heat of formation of naphthalene at 298K was calculated using 298K to be -385.738101kL/mol. The balanced equation for the combustion of naphthalene is:

$$\left(C\_{10}H\_{8}\right)+12\left(O\_{2}\right)\rightarrow 10\left(CO\_{2}\right)+4(H\_{2}0)$$

Hence the enthalpy of combustion of naphthalene was calculated according to the equation:

$$∆H=10E\_{CO\_{2}}+4E\_{H\_{2}0}-E\_{C\_{3}H\_{8}}-12E\_{O\_{2}}$$

The enthalpy of combustion was found to be 4622.450914kJ/mol. The value obtained by experiment is 5154kJ/mol. DFT does not account for the state of the substance as it treats molecules as they would occur under ideal gas conditions. Naphthalene is a liquid at 298K and hence would have potential energy in the form of is van der Waals bonding and intermolecular interactions that would not be accounted for by the DFT calculation, even for thermally corrected values.

### Summary

The enthalpy of combustion under standard conditions for naphthalene and propane was estimated using Hartree Fock and Density Functional Theory techniques. The values were compared with experimental values and attempts were made to explain discrepancies.

Both methods are limited in accuracy by their respective approximations. These approximations can be corrected with further approximation to obtain results more representatives of real physical systems.