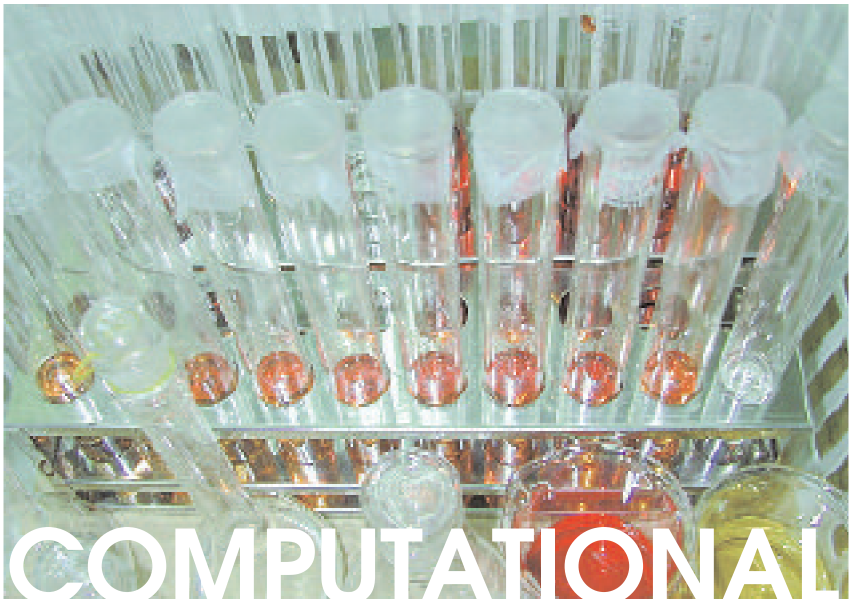

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COMPUTATIONAL THERMOCHEMISTRY

In Support of Calorimetry for Reactive Chemicals Hazard Assessment

Of the multitude of process hazards in the modern chemical industry, the inherent potential energy release from the actual, intended chemical reaction, remains one of the most important. For many chemical reactions, suitable and reliable estimates can be made for the enthalpy release. These methods range from the strictly empirical to the more computationally robust, first principle *ab initio* quantum mechanical methods.

In a typical chemical process design, there are a multitude of Reactive Chemicals hazards which need to be addressed at all stages of the project. These include flammability issues, dust explosion potential, compatibility of inadvertent mixtures, thermal stability, etc. One of the most important parameters in any chemical process is the magnitude of the energy release from the intended chemistry - the heat of reaction. By "intended" chemistry, we mean the chemical reaction that is planned for and desired. The products of this reaction are generally those that will be further reacted in another step or cleaned of impurities (distilled, dried, recrystallized) and eventually sold to the customer.

At a fundamental level, we expect most chemical reactions to proceed "downhill" with a commensurate release of energy. Ignoring the rate of the energy release for the moment, we know that an accurate knowledge of the heat of reaction allows us to determine the potential adiabatic temperature rise in case of a process upset such as loss of cooling to the reactor. Why is this important? Because large magnitude unplanned for temperature increases in process vessels can have deleterious effects such as:
- Emergency relief valves tripping;
- Encountering other degradation chemistries which make the situation even worse;

- Loss of the batch due to side reactions which reduce or eliminate the desired chemistry pathway;
- Raising a solvent above its flash point resulting in a fire.

Determining these heat releases accurately enough to make sound engineering design decisions is thus an important part of the overall hazard evaluation process. In many industrial labs, the approach is two-fold: a theoretical determination or estimate is made of the expected chemistry, and also, if deemed prudent, an experimental determination is made. The next section of this short paper reviews this approach in more detail. Following that, two of the more common predictive tools, CHETAH and the NIST WebBook, are described with particular attention the some newer functionalities of each. Finally, a summary of recent developments in the first principle, quantum mechanical approaches, is given.

Experimental versus theoretical reaction thermochemistry

Using a theoretical approach to reaction thermochemistry has its limitations. Notwithstanding the limitations of applicability of certain prediction methodologies to complex and "unusual" chemistries, often times there are side reactions which might be unknown or ignored by the purely theoretical approach. These undesired reactions might include reactions with the solvent or even interactions with the materials of construction of the reactor. In many cases, but not all, both an experimental value and a prediction of the reaction heat are desirous. Any quantitative calorimetric determination of a reaction heat release must consider a separate analytical determination of the reaction progress (extent) to ensure that the heat value is based on a specific molar conversion. Finally, the purely predictive approach may ignore the important kinetic effects. As an example, a rusting pipe is very "hot" chemistry (hundreds of kcal/mol) but so slow that it is not a hazard. Many of the subsequent ideas are covered in much greater detail in references [1, 2].

Two experimental approaches are typically used in many industrial laboratories to fully understand the scope of the potential chemistries, both desired and undesired. The first approach is to design a calorimetric experiment to determine the reaction thermochemistry for the desired reaction under non-runaway conditions. In other words, the experiment is designed specifically to measure the heat (and possibly the rate) of the desired reaction close to the conditions of the actual process. This value may then be compared to the theoretical prediction and if there is acceptable agreement, then the process engineers and chemists have added confidence in the reliability of their process design.

The other approach is to look at a worst case scenario, typically adiabatic conditions, to determine what the heat (and possibly gas) release may be like if the temperature control to the reactor is lost. In this experimental strategy (typically using an adiabatic calorimeter like the ARC, see reference [3]), both the desired chemistry's heat release is observed along with any exothermic degradation reactions which become kinetically dominant at temperatures above the normal process conditions. In an ARC experiment, pressure is also measured concurrently, adding to the information obtained from the experiment.

In summary, neither the purely predictive approach nor the purely experimental approach may be optimum. Considerations must be made to the scale, types of chemistry being practiced, and known stability hazards of the reaction components in order to plan the optimum hazard evaluation protocol. As an example a "routine" acid catalyzed hydrolysis reaction of an unsubstituted organic ester to the corresponding acid and alcohol, known to be relatively thermoneutral, at say, a one liter scale at a moderate temperature of 50 °C, may require only an estimate of the heat release. If the same ester were substituted with an energetic group like a nitro moiety, an experiment would be certainly justified.

A review of empirical estimation methodologies

A number of semi-empirical, empirical, and first principal methodologies for predicting reaction thermochemistry have been devised over the years. A good summary of these may be found in reference [4].

Certainly, the lowest order approach to this (and typically least accurate) is the bond energy scheme where it is assumed that the reaction heat is simply the difference of the energies of bonds broken and bonds formed.

A more in depth summary with examples of the bond energy approach may be found in reference [5]. The bond energy approach is typically unsuitable for most process design applications due to its inherent inaccuracies.

Many of the successful (i.e. accurate) methods involve group contribution schemes where the molecule is broken down into smaller "pieces", each with a contribution to some property. In this case, the property of enthalpy of formation is the key parameter to the calculation of reaction enthalpy since the reaction heat ($\Delta_{rxn}H$) is determined by the difference between the sum of standard formation enthalpies of products ($\Delta_{prod}H_f^\circ$) and reactants ($\Delta_{react}H_f^\circ$) multiplied by their respective stoichiometric coefficients (α_i, β_i) in the balanced equation.

$$\Delta_{rxn}H^\circ = \Sigma\alpha_i \, \Delta_{prod}H_f^\circ - \Sigma\beta_i \, \Delta_{react}H_f^\circ$$

A highly successful method to determine the enthalpy of formation of a compound, and one commonly used, is Benson's method [6]. This is considered a second order method since each group includes a central atom (or sometimes a group of atoms) and the immediate environment, which is typically all the atoms directly bonded to the central atom. Benson's second-order group contribution method, probably the most successful and widely embraced method, was developed some 37 years ago as an improvement to bond energy (or bond contribution) methods for the prediction of thermochemical properties. This improvement is accomplished by:

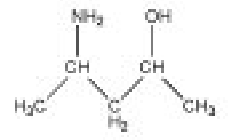
- accounting for the effect of the bonded environment around a group;
- accounting for ring strain effects;
- accounting for isotopic effects (cis/trans, ortho/meta/para);
- accounting for non-bonded interactions (gauche effects).

Benson groups and corresponding contributions to the gas phase enthalpy of formation for the example species 2-amino, 4-hydroxypentane

Benson group	Contribution to Δ_fH° (kcal/mol, 298.15 K)
2 $C-(H)_3(C)$	-10.08x2
1 $C-(H)(C)_2(N)$	-5.2
1 $C-(H)_2(C)_2$	-4.93
1 $C-(H)(C)_2(O)$	-7.2
1 $N-(H)_2(C)$	4.8
1 $O-(H)(C)$	-37.88
Total	*-70.57*

Benson's original notation (shown here) is slightly different than that used in the CHETAH program. The Benson group values were taken from [8]

Consider the example below:



2-amino, 4-hydroxypentane (g)

In general, each multivalent atom must be counted as the central atom in a unique Benson group. Thus in the above case, there are seven multivalent atoms (five carbons, one nitrogen, and one oxygen) and thus we must end up with seven Benson groups. In addition, there may be corrections such as ring strain or other steric effects. Arbitrarily starting from the left, the first carbon is bonded to three hydrogens and one carbon. Thus the Benson group notation is $C-(H)_3(C)$. Note that at the opposite end of the molecule, there is an identical $C-(H)_3(C)$ group. In Benson's original notation, the central, multivalent atom is always listed first, followed by a dash, then everything bonded to that atom is listed the right of the dash. Continuing on, left to right, the next multivalent atom is a carbon, bonded to one hydrogen, two carbons, and a nitrogen. In Benson's notation, this group is then $C-(H)(C)_2(N)$. The next group is a methylene bonded to two carbons. In standard notation, this is $C-(H)_2(C)_2$. The next carbon is bonded to one hydrogen, two carbons and one oxygen: $C-(H)(C)_2(O)$. The amine group is thus $N-(H)_2(C)$ and the remaining hydroxyl group is then $O-(H)(C)$. In this example, there are no corrections such as ring strain or other steric effects.

In the Table, the individual Benson groups are listed for the example along with the corresponding contribution to the gas phase enthalpy of formation. Typically, Benson's method is accurate to ±2-3 kcal/mol for most organic species.

Many sources of Benson groups are available [7]. Most are gas phase contributions but some are condensed phase values for a limited number of groups and hence limited applicability.

In all such approaches to predicting reaction heats, the practitioner mostly relies on choosing a so-called analog reaction which mimics the actual chemical reaction but mostly will not contain the exact species. This is done so that the prediction tools can be applied since in most cases, except for the simplest ones, the thermodynamic data needed for the subject reaction will not exist or even be estimatable (for example a Benson group is not available). The heat calculated for a well chosen analog will generally be close enough for engineering purposes. See [1] for more discussion on this.

The next two sections of this paper briefly review some recent updates to two commonly used tools for reaction thermochemistry: CHETAH and the NIST WebBook.

CHETAH

The computer program CHETAH has been around since the 1970's and was one of the first to implement Benson's method in a relatively easy to use form [8]. Details of the program, including its use for reactive chemicals hazard evaluation beyond the thermochemistry area may be found in reference [9].

Over the years, and under the auspices of the ASTM Committee E-27, the program has been updated, expanded, and made easier to use for reaction thermochemistry. The latest version (8.0) also has a greatly expanded capability to do flammability calculations. Other improvements include an expanded database with approximately 70 new Benson groups added. At present the Benson group database contains about 880 entries.

By far and away, the biggest improvement to CHETAH in the last several years has been the implementation of a Graphical User Interface (GUI) which allows the importation of structures drawn using ChemDraw software [10]. This imported data is then processed without the user needing to choose the molecular fragments that make up the molecule. Also CHETAH has an extensive database of molecules for which the complete necessary thermochemical data are available from the literature for immediate calculations.

The ChemDraw version required for the GUI can be their free version downloadable from their website. Basically the CHETAH program requires a so-called SMILES input which itself is not difficult to master. ChemDraw allows the saving of a structure into the SMILES notation which then may be pasted into the appropriate CHETAH input box.

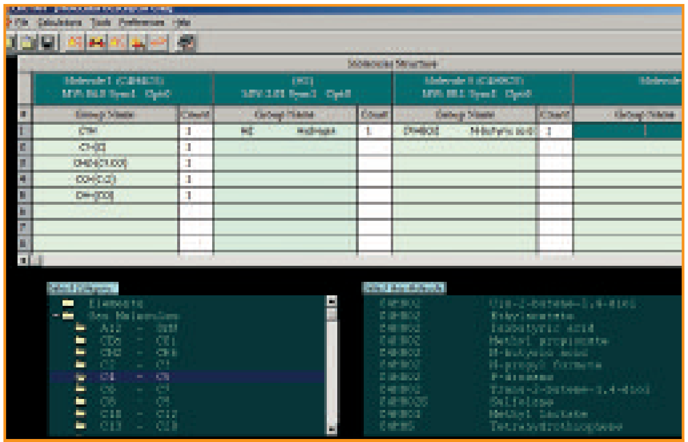
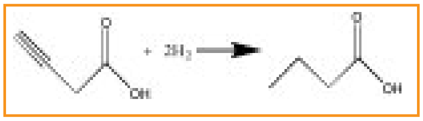


Fig. 1 - The main CHETAH vers. 8.0 screen after the species appropriate for the hypothetical example has been entered. Note that CHETAH uses a slightly modified Benson notation compared to the traditional one shown in the Table

The GUI in CHETAH helps overcome a barrier to the general, occasional user of earlier versions of the program and that is the knowledge of decomposing a structure into Benson's groups. Although not a complicated procedure, if not used frequently, the skill is diminished. Another advantage of this process is that CHETAH automatically helps the user on the occasion that a particular group is not in the database. CHETAH looks for similar groups in its database and allows the user to make a selection if appropriate.

Consider the following hypothetical example, the hydrogenation of 3-butynoic acid:



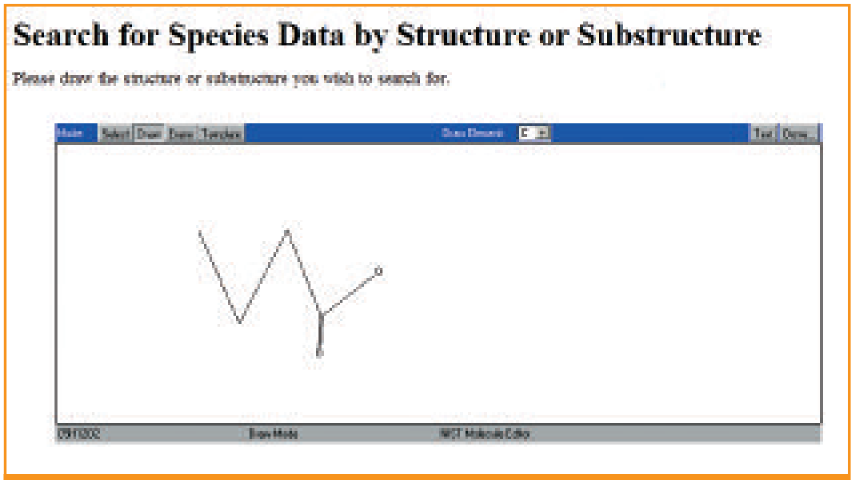
Shown in Figure 1 is the main CHETAH screen after the molecules appropriate to the above reaction have been entered. In this case we entered hydrogen from the elements database in CHETAH and butyric acid from the molecular database. We could have easily built the product from groups.

For reaction thermochemistry, after each species is entered in turn, the user would select the reaction thermochemistry button (the button with arrows pointing in opposite directions). After choosing the reactants, products, and stoichiometry, the reaction heat is then calculated. CHETAH (as in most manifestations of Benson's method) only calculates the heat of reaction in the gas phase. Corrections may need to be applied to the result to determine the heat in any condensed phase. This is discussed in great detail in reference 1. For the above example reaction, the CHETAH result at 25 °C is -73.9 kcal/mol. This is close to the experimentally determined condensed phase result (-69.8 kcal/mol) as found in the NIST WebBook ([11], see next section).

NIST WebBook

For the practitioner of thermochemical predictions, the development of the NIST WebBook (http://webbook.nist.gov/chemistry/) in the last several years has been of great utility. Under the leadership of Dr. Gary Mallard at NIST, this tool has been expanded and a number of enhancements added which aid the thermochemical estimator's abilities. Each will be briefly discussed separately below and include:

- An easy to use GUI for chemical structure input;



Search for Species Data by Structure or Substructure

Please draw the structure or substructure you wish to search for.

Fig. 2 - A screen shot of the GUI in the NIST WebBook, in this case for the molecule butyric acid. Its use is similar to that of the CHETAH interface which uses ChemDraw. As with most GUI's, the hydrogens needed to satisfy the valencies are implied

- A large database of literature thermodynamic properties (mainly experimental);
- A large database of experimentally determined reaction heats;
- The ability of the GUI to deconvolute the structure to Benson groups which then are converted to thermochemical properties including the enthalpy of formation.

The NIST WebBook GUI

The GUI in the NIST WebBook is, like that available to a user of CHETAH, very intuitive and easy to use (see Figure 2 for an example screen shot).

Once the molecule is built in the GUI, several tasks can be performed of relevance to the topic at hand. First, a search can be made in the WebBook's database for all relevant thermochemical data, including published enthalpies of formation and reaction thermochemistry for the species. The reaction data from the literature include any and all reactions in which the species is involved. Typically the list is not too large (unless of course you choose a very common material like water) and often times the reaction of specific interest is included!

By performing a substructure search, data for similar species are often found which may be used in the estimate. As an example, Figure 3 shows the (partial) results of the substructure search of the butyric acid example above.

Each of these links takes the user to the appropriate experimental thermochemistry data compiled in the database. By clicking on the first link (butanoic acid), in Figure 3 the user is taken to a page shown in Figure 4. For the subject at hand, beware that "thermochemistry data" in the NIST database may only mean heat capacity data and not enthalpy of formation (this is quite appropriate in the terminology sense). Clicking on the Reaction Thermochemistry Data link at the page shown in Figure 4 takes us to a reference shown in Figure 5.

In this case we see that the reaction of interest has been measured experimentally and the value is reasonably close to the CHETAH estimate described above. The differences in the heats may be easily explained by the differences in the phases of the various materials. As far as the authors know, there are no immediate plans to add a capability to the tool to be able to search the reaction database for pairs of reactants. This addition, in the authors' opinion, would greatly help those interested in specific classes of chemical reactions.

Another important and useful feature of the WebBook is the ability to draw a species with the GUI and determine the gas phase

Search Results

Due to the large number of matching species, only the first 200 will be shown.

For each matching species the following will be displayed:

- Chemical name
- Chemical formula

Click on the name to see more data.

1. Butanoic acid ($C_4H_8O_2$)
2. γ-Butyrolactone ($C_4H_6O_2$)
3. 4-Methyl-2-oxetanone ($C_4H_6O_2$)
4. Cyclopropanecarboxylic acid ($C_4H_6O_2$)
5. Lithium butyrate ($C_4H_7LiO_2$)
6. Potassium butyrate ($C_4H_7KO_2$)
7. 2-Bromobutyric acid ($C_4H_7BrO_2$)
8. Butanoic acid, 4-chloro- ($C_4H_7ClO_2$)
9. Butanoic acid, 3-chloro- ($C_4H_7ClO_2$)
10. Butanoic acid, 2-chloro- ($C_4H_7ClO_2$)
11. Butanoic acid, methyl ester ($C_5H_{10}O_2$)
12. 4-Hydroxybutyric acid ($C_4H_8O_3$)
13. β-Hydroxybutyric acid ($C_4H_8O_3$)
14. 4-Aminobutanoic acid ($C_4H_9NO_2$)
15. DL-2-Aminobutyric acid ($C_4H_9NO_2$)
16. Butanoic acid, 2-amino- ($C_4H_9NO_2$)

Fig. 3 - A screen shot of the NIST WebBook substructure search result from the structure input in Fig. 2

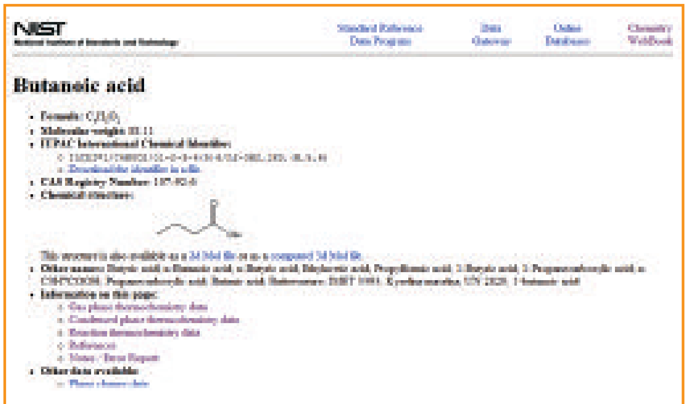


Fig. 4 - A screen shot from the NIST WebBook after clicking on the first entry in Fig. 3

thermochemical properties using its database of Benson groups. Although not as large as the CHETAH database, it is still a convenient functionality to use if the experimental database finds no experimental data.

As an aside, a possible future addition to the NIST WebBook is a database of Reactive Chemicals test data. By test data we mean screening data like DSC and ARC, and possible more scalable tests like VSP and Reaction Calorimetry. It would seem that this is a logical addition to the database and in fact this was a recommendation of the US Chemical Safety Board in their 2002 report [12]. The concept of this database and current progress and plans has been published in [13].

Up to this point in the paper we have discussed some of the more traditional methodologies used by chemists and engineers for predicting reaction thermochemistry. Another method which is employed more frequently in the last approximately ten years in industry is the first principle approach of quantum mechanics. A somewhat dated review of these methods may be found in reference [14]. Once confined to academic practitioners, these methods have become more and more mainstream in the industrial environment. What has driven the increased use of quantum methods is the rapid development of useful methodologies and easy to use software along with the rapid increase in computational "horsepower" as most of these methods are computationally quite intensive. The low end laptop of today has the computational speed and capability of a supercomputer from just a few years ago. Thus the chemical types and species size which these methods are capable of handling is now very pragmatic.

Certainly many of the methods are as accurate or even more accurate than the best group contribution methods.

A review of quantum methods

Ab initio quantum chemistry methods maybe divided into two general approaches, molecular orbital theory based on the Hartree-Fock (HF) model and post-HF treatments, and density functional theory (DFT). The basic techniques have been developed extensively and are described in texts (MO [15, 16]; DFT [16-19]) as well as recent reviews (MO [20, 21]; DFT [22]).

Quantum chemistry methods based on molecular orbital theory represent different approaches to solving the time independent Schrödinger equation. The electronic and nuclear motions are usually assumed to be separable with the Born-Oppenheimer approximation, which implies that the wavefunctions depends explicitly on the electrons but only implicitly on the nuclear coordinates. Since the many body electron problem of the Schrödinger equation cannot be solved directly, approximations are used. The most common of these is the HF approach in which each electron is viewed as interacting with the nuclei and a mean field created by the other electrons. The mean field treatment of the electron interactions ignores energy lowering from instantaneous correlation of the motions of the charged particles. Since the correlation energy can be of the order of energy changes in chemical reactions, higher order treatments are needed for accurate calculations. The simplest improvement is based on Møller-Plesset perturbation theory (MP2, MP3, MP4…). Additional methods are configuration interaction (CI), coupled cluster (CC) methods, and multiconfigurational self-consistent field (MCSCF) theories [21]. Solving the HF equations involves expanding the wavefunction in a series of basis functions (typically Gaussian and plane-wave functions) and projecting the differential equations onto a set of algebraic equations (the Roothan-Hall equations). In general, the quality of a calculation improves with the size of the basis for the wavefunction expansion. The basis sets used in a particular calculation are usually denoted

Fig. 5 - A screen shot of the reaction thermochemistry data in the NIST WebBook after clicking on the corresponding link in Fig. 4

by a series of abbreviations [23] to facilitate comparisons and discussions of electronic structure calculation results. In the limit of an infinite basis set, the numerical approximation converges to the exact solution of the HF equations, termed the Hartree-Fock limit. If increasing treatments of electron correlation are also included, an exact solution to the non-relativistic Schrödinger equation will ultimately be obtained. Increasing accuracy means disproportionately longer computational times; the scaling of HF methods (N^{2-4}, where N is approximately the number of heavy (non-hydrogen) atoms) is much better than that of higher order methods, such as CCSD and QCISD which scales with N^7. As computational costs increase, the feasible molecular size dramatically decreases from about 50-200 to less than ten.

Several approaches have been developed to provide thermochemical estimates with chemical accuracy using fewer computations than would be needed for high order methods and the accompanying large basis sets. Large basis sets are generally needed to realize the benefits of higher order methods. Melius employed the systematic errors in HF and Møller-Plesset perturbation theory to develop a bond additivity correction (BAC) method [24]. The method consists of a relatively fast HF geometry optimization followed by a series of single point energy calculations (frozen geometry) with MPx (x=2 and 4) methods and different basis sets. By performing these calculations for reference compounds with known thermochemical data (typically from experiments), correction factors can be inferred. These may then be used to correct calculated energies for other compounds containing atoms and bonds contained in the reference set. The accuracy of the method is estimated to be ±2 kcal/mol for first and second row elements.

Gaussian theories [25-27], termed as G1 to G3, are other well-developed theories to evaluate molecular energies with chemical accuracy through a series of well-defined calculations. The aim of these methods is to replace one large, intractable calculation with several smaller calculations which can be combined in a specific manner to approximate the desired calculation. The method achieves this by assuming that certain correlation and basis set effects are additive. The G2 and G3 methods have been shown to provide accurate predictions for compounds with second and third row elements. On average, the accuracy for heats of formation of species is around ±1 kcal/mol. In this family of methods, computationally probably the least expensive, and having virtually the same accuracy is the G3MP2B3 method [28] which combines the speed and accuracy of B3LYP hybrid density functional theory for geometry and frequency computations with the rigorous examination of basis set effects on energies of the G3 method. Overall, all G computations are still computationally expensive and have limited use; it is tractable for less than twenty heavy atoms.

Density Functional Theory (DFT) based methods have been used extensively in the solid state community for predicting electronic and optical properties [29], surface reconstructions [30] and more recently surface reactions [31]. The method is founded on the Hohenberg-Kohn theorem which establishes that the ground state energy of a molecule is a functional of the electron density, and the nuclear positions [18]. Most DFT implementations are based on the Kohn-Sham equations and the computational effort typically scales as N^3. However, as one of the most expensive part of the computations is the calculation of Coulomb interactions, there exists potential for the development of new algorithms that scale linearly, *i.e.,* as N [32]. Most modern quantum chemistry packages has some kind of linear-scaling algorithms implemented for DFT which accelerates computations especially for larger molecules (>100 atoms). The lower computational cost of DFT means that useful thermodynamic data can, in principle, be calculated for large molecules and surfaces of interest to many applications. DFT methods have therefore attracted increasing interest as an alternative to the *ab initio* MO approach. However, the theorems which substantiate DFT do not provide a route to the form of the functional of the electron density which gives the ground state energy. Consequently, new functionals which give accurate thermochemical calculations and transition state predictions are important challenges in the development of DFT methods.

Recently developed hybrid functionals, which mix local exchange and correlation functionals with gradient corrections and some component of a Hartree-Fock-like exchange calculation, have been found to be the best current methods for molecular calculations [33-35]. The three parameter hybrid functional, B3LYP [33], has coefficients based upon a best fit to several properties of a large group of small molecules [36]. For small molecules, the hybrid functionals have been

shown to give good results, comparable to or better than MP2 calculations, and in some cases close to the high level G1 and G2 methods [37]. However, there is currently no systematic way of improving the DFT functionals in contrast to the rigorous system of increasing treatment of electron correlation for post-Hartree-Fock (*ab initio*) methods. Consequently, rigorous error checking by comparison to experimental data is necessary when computing previously untested chemistries. This is especially true for transition metal containing molecules. Recent refittings of hybrid DFT parameters to experimental data resulted in a variety of new methods, for reference see [38], some of them a marginally more accurate than the B3LYP method.

Most of these quantum chemistry methods compute single molecule gas phase energetics and thermochemistry. For liquid phase properties, such as vapor pressure, solvation energetics, activity coefficients in mixtures, and miscibility additional techniques are available. A variety of solvation computations are built into many of the packages, the most complete probably is Gaussian-03.

Our primary interest; however, is not species energetics but reactivity which is associated with energetics of chemical reactions. As Melius' work shows, errors may be associated with atoms and bonds. Atomic errors are cancelled in a properly balanced stoichiometric equations. However, bond-errors are not, as bonds change during a chemical reaction. This is where Melius' work becomes very important contribution to quantum chemistry. For elementary reactions, when one or only a few bonds change, errors associated with bonds are minimized.

Applications of the above quantum chemistry methods give molecular energies as a function of the nuclear positions, and thus the 3N-6 dimensional hyper-surface known as the potential energy surface (PES) (*N* is the number of atoms). Equilibrium structures of reactants and products are minimums on this surface, and transition-states are saddle points at passes along the reaction coordinate between reactants and products. Thermodynamic properties, specifically enthalpy, *H*, and entropy, *S*, are needed for understanding reaction mechanisms and estimating reactivity. These thermodynamic variables can be estimated for equilibrium structures by combining the electronic and nuclear energy with zero-point energies (energies of ground state vibrations) and thermal energy. HF and MP2 calculated vibrational frequencies have systematic errors that are often corrected by multiplying the computed frequencies by (0.89 and 0.94), respectively. Scaling factors have also been developed for many of the DFT implementations, but most are near unity and often not invoked. The optimal scale factors vary by basis set and the data set used to determine the fit. Finite temperature thermodynamic properties may be calculated based on standard statistical mechanics equations for including translational, rotational, and vibrational energies (electronic thermal energy corrections are typically ignored) [39].

As mentioned earlier, most modern quantum chemistry packages, either academic or commercial codes, contain a variety of methods of MO theory and DFT. Many of them are capable to perform large-scale computations as distributed computing became cheaper and more widespread. The most popular commercial packages are equipped with sophisticated graphical user interfaces that include molecule/orbital visualizer, molecule editor, and job submitter. A short list of these includes Gaussian Inc.'s Gaussian-03 package, Schrödinger Inc.'s Jaguar package, Wavefunction's Spartan04, Accelrys' DMOL/Materials Studio, Qchem Inc.'s Qchem. Notably, PCSpartan-04 runs very effectively on laptop and desktop computers, it is interfaced to the Cambridge Crystallography Database, and

RIASSUNTO

Termochimica computazionale. Un aiuto per la valutazione del rischio chimico

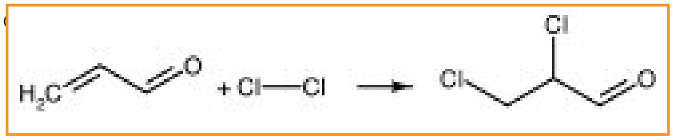
Tra i rischi di processo insiti nell'industria chimica, quello relativo al rilascio dell'energia potenziale di una reazione chimica è senz'altro tra i principali. Per molte reazioni chimiche possono essere effettuate delle previsioni adeguate e attendibili di rischio attraverso il calcolo del rilascio entalpico, che può essere condotto mediante un procedimento strettamente empirico o utilizzando metodi computazionali, soprattutto quelli quanto-meccanici ab initio.

to an internal database containing large number of pre-computed molecules. Its speed, ease of use, and wide features makes it attractive for everyday use by experts of other fields. Among academic, and semi-commercial codes (meaning non-profit license) several packages are available, most of them lacks graphical user interface that limits their wider usability. Nevertheless, their speed and capabilities many times overcome commercial codes. A short list includes GAMESS from Iowa State University, Molpro by University College Cardiff Consultants Ltd., ACES-II from the University of Florida, NWChem from the Pacific Northwest National Laboratory, Turbomole from the University of Karlsruhe and PQS from Parallel Quantum Solutions. In general, this latter class needs more computer expertise to operate comparing to programs with graphical user interfaces.

Most of these quantum chemistry methods compute single molecule gas phase energetics and thermochemistry. For liquid phase properties, such as vapor pressure, solvation energetics, activity coefficients in mixtures, and miscibility additional techniques are available. A variety of solvation computations are built into many of the packages, the most complete probably is Gaussian-03 with respect to polarizable continuum models [40]. In the last decade one notable method has been developed by Andreas Klamt [41], and the CosmoTherm program package commercialized by CosmoLogic Gmbh. This is the only *ab initio* quantum chemistry based program currently that gives a comprehensive set of liquid phase properties directly applicable to engineering. Its use and applicability has been steadily increasing starting from vapor-liquid equilibria, solubility of gases, solids, activity coefficients, to physiological partitioning. For references see http://www.cosmologic.de.

Quantum chemistry example

The estimation of heat of reaction between acrolein and chlorine to form 2,3-dichloro-propanal became important for process development purposes. The reaction is highly exothermic, consequently an accurate reaction heat is necessary for proper sizing



According to an internal Dow data base, the heats of formation of liquid acrolein and DCP are -22.04 kcal/mol and -78.91 kcal/mol, respectively, resulting in a standard heat of reaction with chlorine gas of -56.86 kcal/mol. However, the heat of formation of DCP in this database is merely an estimate of unknown accuracy. Other literature sources also showed quite large deviations [42, 43], consequently, parallel experimental and theoretical studies were undertaken to find accurate heats of reaction and heats of formation. Since we are dealing with relatively small molecules, it is computationally effective to perform high level, more accurate computations at the G3MP2B3 level. The reaction heat was computed as -44.3 kcal/mol, and calorimetric experiments showed a reaction heat of -44.4 ± 0.9 kcal/mol in excellent agreement. The origin of discrepancy is the heat of formation of acrolein, -19.55 kcal/mol [42] while the high-level quantum chemistry method produced -15.32 kcal/mol. Further computations at the G2 and G3 levels all resulted in the -15.3 kcal/mol range within 0.2 kcal/mol. Comparing the performance of the quantum method for other molecules in the same family, we believe, that the computed data are more accurate than the literature values. On the basis of the calorimetric experiments and computations we recommend the gas

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