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Sources of uncertainty of thermodynamic and reaction kinetic parameters

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Experimental sources (thermodynamics and kinetics)

natural uncertainty of measurements

Theoretical sources

thermodynamics:

ab initio – all quantum chemical methods are approximate

group additivity – an interpolation scheme with inherent errors

kinetics:

ab initio error due to approximations

reaction kinetics model

contains non-measurable and non-calculable parameters

Active Thermochemical Tables

Active Reaction Kinetics Tables



Thermodynamic data

In combustion modeling they are used in calculating
Equilibrium constants

$$K_r = \exp(-\Delta_r G/R T) = \exp(\Delta_r H/R T - \Delta_r S/R)$$

Heat production

$$\Delta_r H$$

Rate constants from those of reverse reactions

$$k_{\text{fwd}} = K_r k_{\text{rev}}$$

Tabulated data

Standard enthalpy of formation, $\Delta_f H^0$

Standard entropy of formation, $\Delta_f S^0$

Specific heat capacity, $C_p(T)$

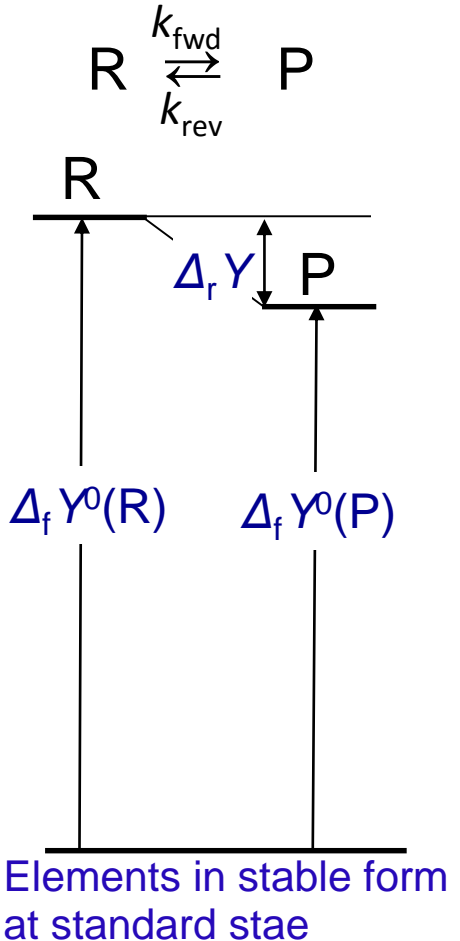
Sources of data

Experiments

Ab initio calculations

Empirical schemes based on

observed rules in experimental or ab initio data



$$\Delta_r Y = \Delta_f Y^0(P) - \Delta_f Y^0(R)$$

Experimental sources of thermodynamic data

Enthalpy of formation, $\Delta_r H$

Determine the enthalpy change of any reaction $\Delta_r H$

Calculate enthalpy of formation from $\Delta_r H$

and those of known reaction partners

$$\Delta_f H^0(R) = \Delta_r H + \Delta_f H^0(P)$$

Entropy of formation, $\Delta_r S$

Rarely measured directly

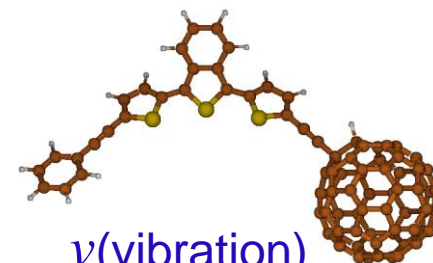
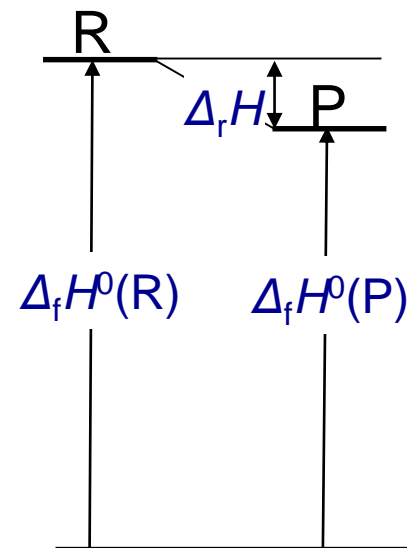
(from temperature dependence of K_r)

Calculated from experimental molecular parameters
using statistical thermodynamics

Specific heat capacities, C_p

Can be measured directly for stable species

Calculated from experimental molecular parameters
using statistical thermodynamic



ν (vibration)
 Θ (inertia)

generally simplified
formulas of statistical
thermodynamics

Experimental methods for measuring reaction enthalpies

Calorimetry

The most accurate method to measure reaction enthalpy

Spectroscopy

For bond dissociation

Gas-phase acidity from negative ion photodetachment

Appearance potential of ion pair formation

UV absorption spectroscopy

Reaction kinetics

For unstable species

Determine the equilibrium constant via measurement of forward and reverse rate coefficients

$$K_r = \exp(-\Delta_r G/R T) = \exp(\Delta_r H/R T - \Delta_r S/R)$$

Electrochemistry

measure $\Delta_r G$ through electrode potential

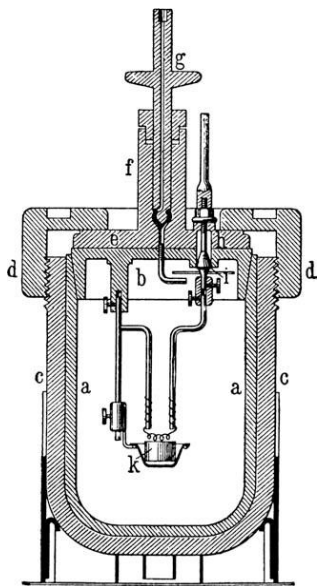
Experimental methods for measuring reaction enthalpies

Calorimetry

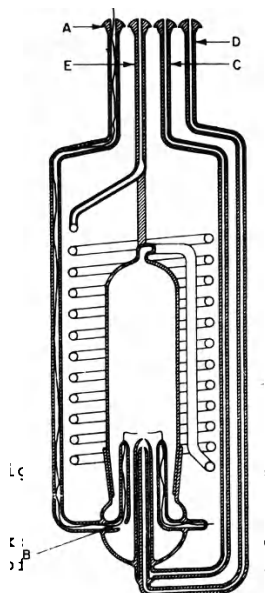
the most accurate method to measure enthalpy changes
was used to measure the most probably most accurately known thermodynamic
property: C_p of water – 0.001%
reaction enthalpy is observed as
temperature change
phase change, e.g. ice to water

Mostly Combustion Calorimetry

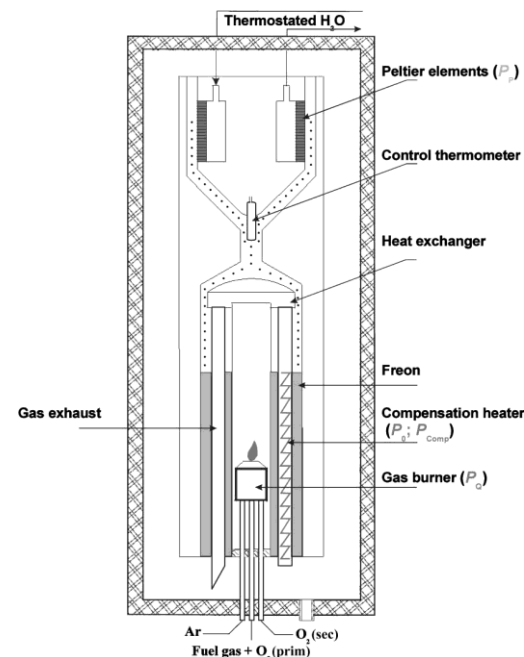
Berthelot's bomb calorimeter



Rossini's flame calorimeter



Modern design



Combustion Calorimetry

Sources of error

uncontrolled heat loss or gain

sample purity

sample quantity

measurement of temperature

amount and identity of products (especially if heteroatoms N,S,Hlg present)

sample holder corrosion

calibration

Accuracy (standard: 95% confidence, introduced by Rossini)

0.01% for CHO compounds

0.05% for more complex molecules

0.01% high quality commercial equipment

0.5-1% average commercial equipment

Examples:

Ethylene oxide 1306.0 ± 0.6 kJ/mol

but

dibenzo-*p*-dioxin 59.2 ± 4.4 kJ/mol (1999) and 50.1 ± 2.2 kJ/mol (2002)

Nonexperimental methods for getting reaction enthalpies

Ab initio quantum chemistry

Solving the Schrödinger equation for a molecule provides its energy and its thermodynamic properties

In principle.

In fact, the methods of ab initio quantum chemistry are approximate

Estimation of thermodynamic parameters based on empirical rules

Group additivity method

Ab initio methods

are based on a few approximations

and a real effort to fix the problems of the approximations

Group additivity

within certain limits of accuracy the thermodynamic properties of properly selected groups add up to that of a molecule

data can be borrowed from information on one or more similar molecules

the question is the “limit of accuracy”.

Nonexperimental methods for calculating reaction enthalpies

Ab initio methods

are based on a few approximations
and a real effort to fix the problems of the approximations

There is a hierarchy of approximations in routine methods

1. one solves the nonrelativistic Schrödinger equation for the electrons + atomic nuclei system
2. Born-Oppenheimer approximation: electrons and nuclei treated separately
 - a. solve the electron Schrödinger equation for electrons at fixed nuclear separation (=calculate the potential energy surface)
 - b. solve the nuclear Schrödinger equation (done with approximations)
3. The electronic Schrödinger equation is solved using the one-electron approximation each electron occupies an orbital that is determined by the attraction by the atomic nuclei and the repulsion by the average charge density of the other electrons occupying their own orbitals
 - involves calculation of numerous integrals in space
 - a very useful principle, matches and helps chemists' thinking
 - is generally referred to as Hartree-Fock or simply SCF method
 - what is missing is the electron correlation
4. The one-electron orbitals are represented as linear combinations of numerically generated atomic orbitals, AOs (or plane waves in solid state)
AO basis should be 'complete' – infinite number of orbitals

Errors of relative energy in ab initio calculations

Size of error

roughly scales with number of electrons

basis set size approximation

tens of kcal/mol

electron correlation

tens of kcal/mol

Corrections

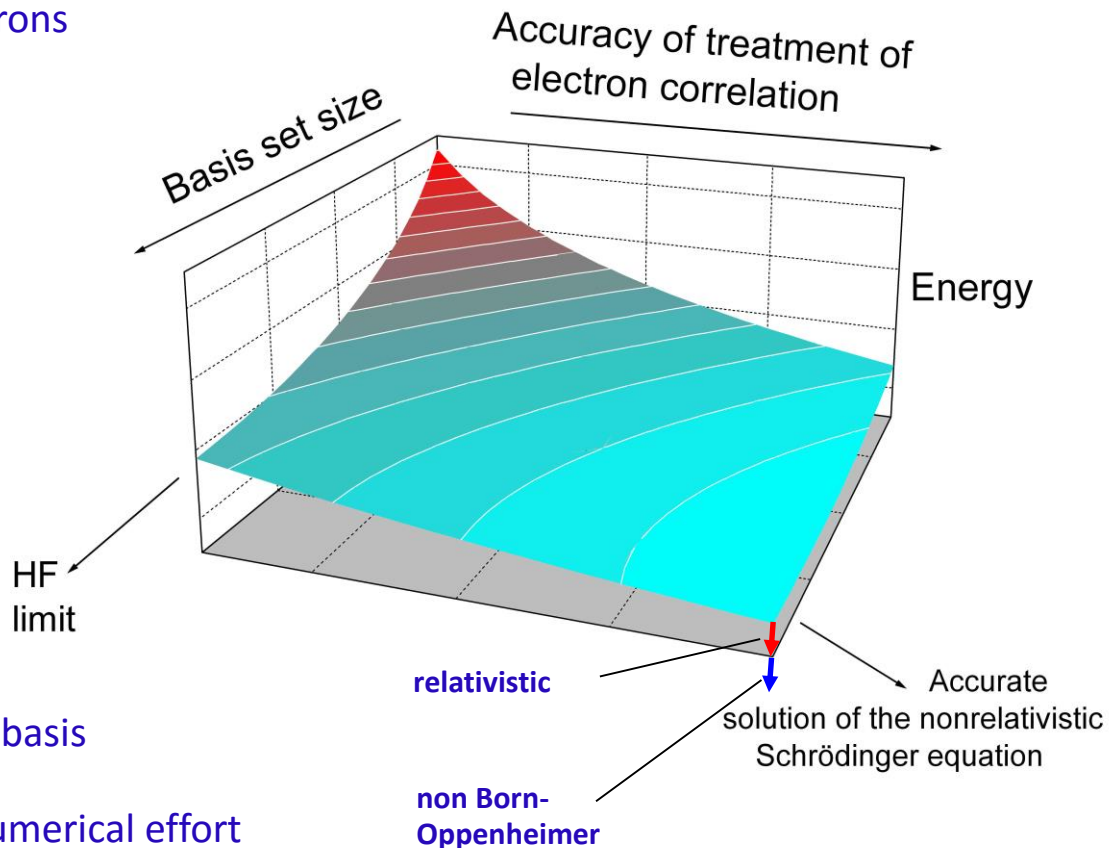
Routine level

1. for basis set incompleteness
useless without correcting
for electron correlation
slow convergence with
basis set size

2. for missing electron correlation
meaningful with large enough basis
basis set error
very slow convergence with numerical effort

Very accurate level

3. for nonrelativistic effects
4. for non-Born-Oppenheimer effects
magnitude of correction: below 1 kJ/mol



Extended Pople Diagram

Errors of enthalpy in ab initio calculations

Nuclear Schrödinger equation

vibrational frequencies

a few % error

zero-point energy

kcal/mol error

C_p , S

kJ/mol/K

For simple systems very good

theory/experiment agreement

match without corrections

e.g. D_0 for H_2 :

36 118.0696(4) cm^{-1} (exp)

36 118.0695(10) cm^{-1} (theory)

Corrections

Scaling vibrational frequencies, anharmonicity

Low-level ab initio methods

can be “calibrated” using empirical thermochemistry data

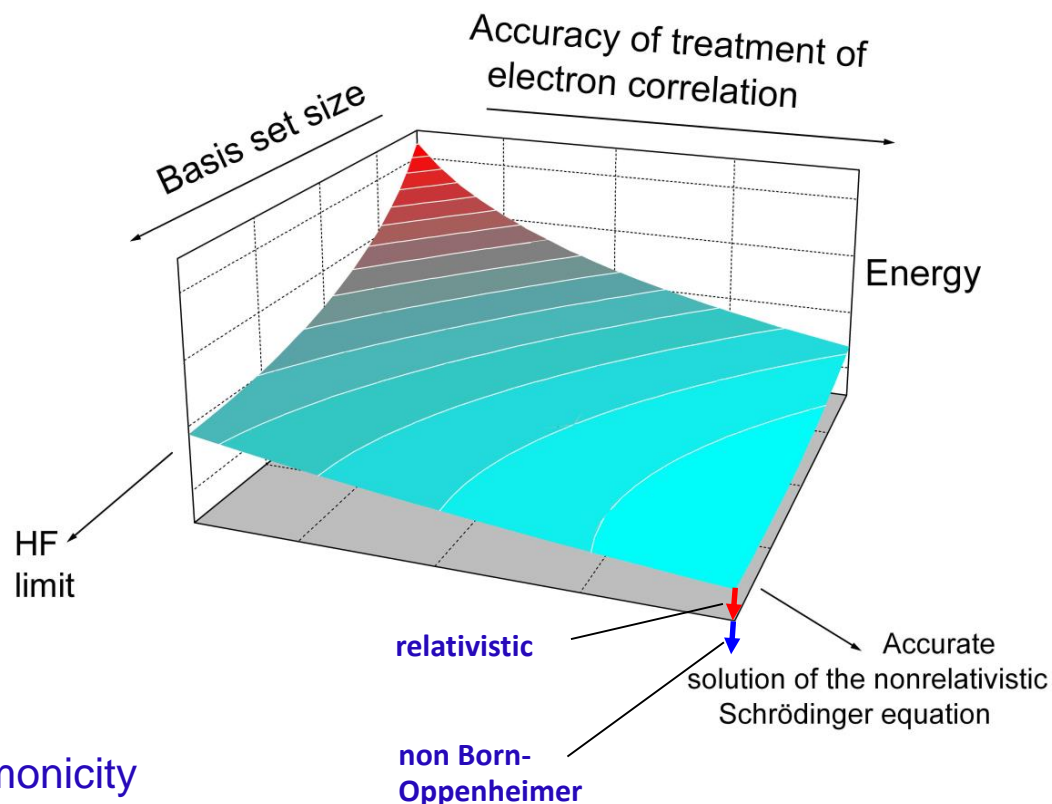
isodesmic reactions

hypothetical reactions retaining the types and number of each type of bonds

error cancellation

No quantum chemistry method provides general rules

data need to be handled the same way as experimental ones



Nonexperimental methods for calculating reaction enthalpies

Group additivity (GA) schemes

Chemistry – almost additive properties

strictly additive is only mass

No theoretical foundation

can be based both on experimental and ab initio data and on combinations thereof

Approximate additivity of energy contributions

bonds – limited (many kJ/mol error)

groups – much better (several kJ/mol error)

groups in different environments (a few kJ/mol)

additional corrections (down to 1 kJ/mol)

Corrections are generally successive

new corrections extend the set of existing Group Values (GV)

no retrospective modifications

Corrections apply to different groups of compounds

generally can not be combined before error check

Extreme values of the GA scheme

quick

more reliable than blindfolded application of quantum chemistry

at the price of human effort

when done with care, can compensate experimental errors

Reaction kinetic data

Rate coefficients and their pressure and temperature dependence

The basic quantities in combustion modeling

Sources of information on rate coefficients and the error sources

Experiment

- direct measurement

 - down to <10% error

 - extreme effort and care

 - often done with simplifying approximations (pseudo first order etc.)

 - evaluation can be rather involved if a complex scheme needs to be fitted

- relative measurement

 - carries error of rate coefficient of reference reaction

- combination of information from different kinds of direct experiments

 - offers consistency

- combination of data from a wide range of kinetics experiments

 - even more consistency

Limitation

- experiments can be performed only in limited temperature and pressure ranges

Extrapolation

- bimolecular reactions

 - no pressure dependence

 - Arrhenius form

- unimolecular reactions

 - empirical pressure dependence + Arrhenius temperature dependence

Sources of information on rate coefficients and the error sources

Extrapolation of rate coefficients

Routine methods

bimolecular reactions

no pressure dependence

Arrhenius form for temperature dependence

unimolecular and complex-forming bimolecular reactions

Arrhenius form + empirical pressure dependence formulas

Errors magnified

The Arrhenius form is often not applicable

more general (Aquilanti et al., CPL **498**, 209)

$$k(T) = A \left(1 - d \frac{\varepsilon}{RT} \right)^{\frac{1}{d}} \quad \text{based on} \quad \exp(x) \equiv \lim_{n \rightarrow \infty} \left(1 + \frac{x}{n} \right)^n$$

$$\ln k(T) = \ln(A) + \frac{1}{d} \ln \left(1 - d \frac{\varepsilon}{RT} \right) \quad \text{more flexible than Kooij's} \quad k(T) = A + \frac{B}{T} + \exp \left(-\frac{\varepsilon}{RT} \right)$$

May be extended further

$$\ln k(T) = \ln(A) + \frac{1}{c} \ln \left(1 - d \frac{\varepsilon}{RT} \right)$$

Sources of information on rate coefficients and sources of their error

Extrapolation of rate coefficients using theory

Need to be done for each temperature, pressure separately

Bimolecular reactions

modeling simple except for tunneling

(variational) Transition State Theory (TST) based on ab initio information carries (and magnifies) the error of the ab initio source

+ adds more because of inadequacy of TST

Unimolecular reactions with a tight barrier

Accurate modeling somewhat more complicated

TST + Master Equation modeling for energy transfer

additional error due to inadequacy of energy transfer model + parameters for calibration, experimental data needed

with that, very good reproduction of experimental data

Prediction?

Complex-forming bimolecular reactions and unimolecular dissociation

accurate modeling requires expertise and care

variational RRKM for rate coefficients of unimolecular steps

Master Equation modeling involving multiple potential wells

not predictive without experimental scaling points

New paradigm:

error estimate by Monte Carlo variation of TST and energy transfer parameters

Modeling can wash out limits between equilibrium and non-equilibrium situations

Consistency of data

Thermochemistry

demand raised decades ago

different solutions in different fields:

gas-phase kinetics, organic chemistry, metallurgy

Kinetics

the Prime concept

Designed with engineering target

Overall consistency with physical meaning

Active Thermochemical Tables, ATcT (Ruscic)

1. develop Thermochemical Networks (TN) including reactions with all possible reactions connecting chemical species
2. include all thermochemistry information including experiment and theory
3. do an overall fitting, readjust error bars on the fly (reduces weight of data not matching the rest of data in the TN)

produces a global set of enthalpies of formation

so consistent that data are used for benchmarking the highest-level ab initio methods

Active reaction kinetics database (Turányi)

the Prime concept and the ATcT concept combined

1. develop reaction kinetic networks including all reasonable reactions
 2. include all *reliable* measurement data as detailed as time dependence of measured signal
 3. do an overall fit with estimated weighting based on declared or estimated error
- produces a global set of rate coefficients that are consistent with the thermochemistry

CONCLUSION

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DO WE WANT ANYTHING MORE?