THERMOCHEMISTRY of CHEMICAL REACTIONS:
NOMENCLATURE, SYMBOLS and EXPERIMENTAL METHODS for
the DETERMINATION of BOND ENERGIES*

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Introduction

Thermochemistry has been defined in one of the most popular physical chemistry textbooks as “the study of heat produced or required by chemical reactions” [1]. The use of ‘heat’, instead of the more general word ‘energy’, immediately suggests a close association between thermochemistry and calorimetry – the oldest experimental technique that allows to investigate the thermodynamics of chemical reactions. Thermochemistry, which was founded in the 18th century by Black, Lavoisier, and Laplace, has seen few major developments since the days of Berthelot and Thomsen, over 100 years ago [2]. However, the golden years of calorimetry started in the 1930’s, thanks to the work on organic compounds by Rossini and his colleagues at the National Bureau of Standards [3], and continued to the 1960’s and 1970’s. Thermochemistry studies of organometallic compounds were pioneered by Skinner and his coworkers at Manchester University [4,5].

Molecular energetics (or molecular thermochemistry) is concerned with the study of the thermodynamic stability of molecules and chemical bonds, and therefore the information it provides is crucial for many areas in chemistry. The energy of a chemical species is closely related to the structure and reactivity of that species and a detailed understanding of these relationships is being pursued by many research groups around the world.

‘Classical’ calorimetry, in its several forms, has been the main source of energetic data, such as enthalpies of formation, of reaction, and of phase transition. Its main limitation is, however, that it can only be used to the study of thermochemistry of long-lived molecules, i.e. those species that

can be isolated, purified and kept in a reaction vessel, whereas modern chemical research often involves short-lived molecules, neutral or ionic, in solution or in the gas phase. It is therefore not surprising that a variety of techniques to probe the energetics of these transient species have been developed in the last two decades.

The correct relationships between the quantities measured with some of the newer techniques and thermodynamic functions are often not straightforward and deserve a careful analysis, since many of the scientists that have developed and use those techniques have not been trained as chemical thermodynamicists and some are not particular alert to that issue. This task will be completed in the near future [6].

Nomenclature and symbols for ‘bond energies’ are, at the moment, somewhat confusing. However, these quantities are now widely used to estimate the thermochemistry of chemical reactions involving species for which the standard enthalpies of formation are unknown. The proliferation of designations and symbols, such as bond strengths, bond enthalpies, bond energies, bond dissociation enthalpies, bond enthalpy terms, stepwise bond dissociation energies, intrinsic bond energies, clearly requires some standardisation.

The first part of this report discusses the meaning, designation, and symbols of the different parameters used in molecular thermochemistry studies. The second part includes a brief description of the main experimental methods that have been used to derive data, together with a detailed analysis of their basic assumptions and how thermodynamic quantities are obtained. Rather than describing experimental set-ups, we will concentrate on a few topics that are relevant to consider when using or discussing data obtained through each method.

**PART I  Nomenclature, symbols and definitions**

Nomenclature and symbols for chemical thermodynamics, recommended by the International Union of Pure and Applied Chemistry (IUPAC) through the Commission on Physicochemical Symbols, Terminology and Units [7] and the Commission on Thermodynamics [8] will be adopted here. For example, the usual symbols $U$, $H$, $G$, $S$, and $C_p$ will be adopted for internal energy, enthalpy, Gibbs energy, entropy, and heat capacity at constant pressure, respectively. A change in these thermodynamic quantities is indicated by using the symbol $\Delta$ followed by a subscript (specifying the process to which the quantity refers). For instance, a reaction Gibbs energy is represented by $\Delta_r G$, a combustion enthalpy by $\Delta_c H$, a solution enthalpy by $\Delta_{sol} H$, a vaporization entropy by $\Delta_{vap} S$, and so on. Standard states will be denoted by the superscript $^o$, as in $\Delta_r H^o$ (H$_2$O, l), the standard enthalpy of formation of liquid water.

No symbol has been approved by IUPAC for ‘dissociation energy’ in the chemical thermodynamics section of reference 7. Under “Atoms and Molecules”, either $E_d$ or $D$ is indicated. The latter is more common and IUPAC recommends $D_0$ and $D_e$ for the dissociation...
energy from the ground state and from the potential minimum, respectively. We will use $D_{U,m}^\circ(T)$ for a bond dissociation internal energy and $D_{H,m}^\circ(T)$ for a bond dissociation enthalpy, both at a temperature $T$. (Often $DU^\circ_T$ and $DH^\circ_T$ are used in the literature but these symbols are not to be encouraged because of the possible confusion with the product of $D$ and $U$ or $D$ and $H$, respectively; in general physical quantities should always be represented by single letter symbols). In cases where it is clear that the temperature refers to 298.15 K, the ‘$T$’ will be omitted. As the ‘bond energy’ concept can be explored in a variety of ways, some extra names and symbols are required.

1. Bond Energies

Although standard enthalpies of formation provide information about the net stability of molecules and their transformations, they do not always indicate stability of individual bonds. This analysis normally involves parameters, loosely called ‘bond energies’, which reflect the amount of ‘energy’ required to cleave chemical bonds. The literature is plagued with a variety of concepts that fall into that designation but are not always synonymous. We can find names like bond strengths, bond enthalpies, bond energies, bond dissociation enthalpies, bond dissociation energies, bond disruption enthalpies, bond enthalpy terms, intrinsic bond energies, and symbols like $D$, $\bar{D}$, $\langle D \rangle$, $E$, BDE, etc. The meaning of these concepts is not always obvious and, unfortunately, some are occasionally misused. These concepts are discussed in the following paragraphs. All quantities considered here are molar quantities and so the subscript ‘m’ will be omitted.

Bond dissociation enthalpies and energies

For a molecule AB, where A and B can be atoms or groups of atoms, the A−B bond dissociation enthalpy, represented by $D_{H}^\circ (A−B, T)$, is defined as the standard enthalpy of the gas phase reaction where the only event is the cleavage of that bond, at a given temperature:

$$AB(g) \rightarrow A(g) + B(g)$$

The A−B bond dissociation energy, on the other hand, is the standard internal energy of reaction (1). It will be abbreviated by $D_{U}^\circ (A−B, T)$ and its relation with $D_{H}^\circ (A−B, T)$ is given by

$$D_{U}^\circ (A−B, T) = D_{H}^\circ (A−B, T) - RT$$

As stated above, the symbol ‘$T$’ will be omitted whenever the temperature refers to $T = 298.15$ K. In this case,

$$D_{U}^\circ (A−B) = D_{H}^\circ (A−B) - 2.48 \text{ kJ mol}^{-1}$$

and

$$D_{H}^\circ (A−B) = \Delta_r H^\circ (A, g) + \Delta_r H^\circ (B, g) - \Delta_r H^\circ (AB, g)$$
There are plenty of publications where the standard enthalpy of reaction (1) is called ‘bond
dissociation energy’, and abbreviated by BDE or by \( D(A-B) \). However, this designation (as well
as the abbreviations) can be misleading and we favor the nomenclature indicated above. It should
also be recalled that the International Union of Pure and Applied Chemistry (IUPAC)
recommends \( D_0 \) for the dissociation energy at \( T = 0 \) K [therefore, \( D_0 = D_0^o (0 \text{ K}) = D_e^o (0 \text{ K}) \)] and \( D_e \) for the hypothetical dissociation energy from the potential minimum [7].

Having in mind that a bond dissociation enthalpy is simply the standard enthalpy of a particular
reaction, the relationship between two values of \( D_0^o (A-B, T) \) at different temperatures is easily
obtained as:

\[
D_0^o (A-B, T) = D_0^o (A-B, 0 \text{ K}) + (H_T^o - H_0^o)_A + (H_T^o - H_0^o)_B - (H_T^o - H_0^o)_{AB} \tag{5}
\]

Note that, at \( T = 298.15 \text{ K} \), \( D_0^o (A-B) > D_0^o (A-B, 0 \text{ K}) \), because the sum of the last three terms
in equation (5) is positive.

In order to distinguish solution from gas phase bond dissociation enthalpies, we shall use the
subscript ‘sln’. Namely, \( D_{0,\text{sln}}^o (A-B, T) \) represents the standard enthalpy of the reaction in
solution, where the only event is the cleavage of the A–B bond, at a given temperature:

\[
\text{AB(sln)} \rightarrow \text{A(sln)} + \text{B(sln)} \tag{6}
\]

The relationship between \( D_0^o (A-B) \) and \( D_{0,\text{sln}}^o (A-B) \) is given by equation (7) (as usual, we have
dropped the symbol ‘\( T \)’ to indicate that the temperature is 298.15 K). \( \Delta_{\text{solv}}^o H^o \) are the standard
enthalpies of solvation of reactants and products

\[
D_0^o (A-B) = D_{0,\text{sln}}^o (A-B) + \Delta_{\text{solv}}^o H^o (\text{AB}) - \Delta_{\text{solv}}^o H^o (A) - \Delta_{\text{solv}}^o H^o (B) \tag{7}
\]

Equation (7) indicates that \( D_0^o (A-B) = D_{0,\text{sln}}^o (A-B) \) when the solvation terms cancel out.

**Stepwise and mean bond dissociation enthalpies**

Experimental values of bond dissociation enthalpies are scarce compared with the data available
for standard enthalpies of formation. This is not surprising because most chemical reactions that
have been studied thermochemically involve the cleavage and the formation of several
bonds. The measured standard reaction enthalpies are thus enthalpy balances of various bond
dissociation enthalpies, whose individual values are often unknown.

If we consider the molecule \( \text{AB}_n \), where A is an atom and B is an atom or a chemical group, we
can define \( n \) \( A-B \) bond dissociation enthalpies, each one represented by \( D_{0,\text{i}}^o (A-B) \), where \( i = 1, \ldots, n \), according to the processes below. The only event in each reaction is the cleavage of one
bond, at a given temperature:

\[
\begin{align*}
\text{AB}_n(g) &\rightarrow \text{AB}_{n-1}(g) + \text{B}(g) & D_{0,1}^o (A-B) = D_{0}^o (\text{AB}_{n-1}-\text{B}) \tag{8} \\
\text{A–B}_{n-1}(g) &\rightarrow \text{A–B}_{n-2}(g) + \text{B}(g) & D_{0,2}^o (A-B) = D_{0}^o (\text{AB}_{n-2}-\text{B}) \tag{9} \\
\cdots & & \cdots \tag{10}
\text{A–B}(g) &\rightarrow \text{A}(g) + \text{B}(g) & D_{0,n}^o (A-B) = D_{0}^o (A–B) \\
\end{align*}
\]
These are, respectively, the first, the second, ..., and the nth bond dissociation enthalpies in the molecule \( \text{AB}_n \), and are called stepwise bond dissociation enthalpies.

If, however, we consider the process

\[
\text{AB}_n(g) \rightarrow \text{A}(g) + n\text{B}(g) \tag{11}
\]

the enthalpy of this reaction, \( \Delta_r H^o \), is the sum of \( n \) A–B bond dissociation enthalpies, and the ratio \( \Delta_r H^o / n \) represents the average enthalpy of cleavage of the A–B bond. It is called the mean bond dissociation enthalpy (also known as mean bond disruption enthalpy) and it is represented by \( \overline{D^o_{\text{H}}} \) or by \( \langle D^o_{\text{H}} \rangle \) (the symbol we will adopt).

Let us conclude by giving, for the sake of clarity, the most general definition of mean bond dissociation enthalpy. For any molecule \( \text{AY}_m\text{X}_n \), where \( \text{A} \) is a central atom and \( \text{X} \) and \( \text{Y} \) are any mono- or polyatomic groups, the A–X mean bond dissociation enthalpy is defined as \( 1/n \) times the enthalpy of reaction (12) at \( T = 298.15 \) K:

\[
\text{AY}_m\text{X}_n(g) \rightarrow \text{AY}_m(g) + n\text{X}(g) \tag{12}
\]

\[
\langle D^o_{\text{H}} \rangle \text{ (A–X)} = \frac{\left[ \Delta_r H^o (\text{AY}_m, g) + n\Delta_r H^o (\text{X}, g) - \Delta_r H^o (\text{AY}_m\text{X}_n, g) \right]}{n} \tag{13}
\]

If \( \text{A} \) is bonded to a single type of ligand, as in \( \text{AX}_n \), then

\[
\langle D^o_{\text{H}} \rangle \text{ (A–X)} = \frac{\left[ \Delta_r H^o (\text{A}, g) + n\Delta_r H^o (\text{X}, g) - \Delta_r H^o (\text{AX}_n, g) \right]}{n} \tag{14}
\]

For example, in the case of methane, where all the bonds are equivalent, the total bond enthalpy will be equal to the enthalpy of atomization (\( \Delta_a H^o \); see below) of methane, and the mean bond dissociation enthalpy will be one quarter of this. The enthalpy of atomization of methane is \( \Delta_a H^o (\text{CH}_4, g) = 1663.1 \text{ kJ mol}^{-1} \) and therefore the mean C–H bond dissociation enthalpy is \( \langle D^o_{\text{H}} \rangle \text{ (C–H)} = 415.78 \text{ kJ mol}^{-1} \). The stepwise C–H bond dissociation enthalpies are \( D^o_{\text{H}} \text{ (C–H)} = 435.14 \text{ kJ mol}^{-1} \), \( D^o_{\text{H}} \text{ (C–H)} = 444.50 \text{ kJ mol}^{-1} \), \( D^o_{\text{H}} \text{ (C–H)} = 444.50 \text{ kJ mol}^{-1} \) and \( D^o_{\text{H}} \text{ (C–H)} = 338.90 \text{ kJ mol}^{-1} \).

Finally, it is noted that the concepts of mean and stepwise bond dissociation enthalpies can also be defined in solution.

**Bond enthalpy contributions and bond strengths**

Replacing stepwise bond dissociation enthalpies by mean bond dissociation enthalpies and ‘transferring’ bond dissociation enthalpies from one molecule to another can be dangerous, leading to substantial errors. Yet, this error cancels out if the same procedure is applied to derive relative bond dissociation enthalpies in a series of similar compounds.

There are alternative ways of looking into the previous problem, which are closer to the idealized concept of a chemical bond strength. Consider reaction (15), where all the metal-ligand (M–L and M–X) bonds are cleaved simultaneously. The enthalpy of this disruption reaction at \( T = 298.15 \) K can be calculated by using enthalpy of formation data as a sum of \( n \) M–L and one M–X bond enthalpy contributions (equation 16).


ML\textsubscript{n}X (g) → M(g) + nL(g) + X(g) \quad (15)

$$\Delta f H^\circ = nE(M-L) + E(E-X)$$ \quad (16)

**Bond enthalpy contributions**, also named **bond enthalpy terms**, which we will represent by $E$, have been used to investigate the bonding energetics of many molecules, including organometallic complexes. The case of metal-ligand bonds in substituted metal-carbonyl complexes was first discussed by Skinner, Pilcher, and Connor [9,10].

Apparently, there is not much advantage in using bond enthalpy contributions to discuss bonding energetics in a series of similar complexes. Nevertheless, besides emphasizing that the absolute values so obtained should not be regarded as bond dissociation enthalpies, the bond enthalpy contribution concept attempts to consider a pertinent issue in molecular energetics: the **transferability** of bond enthalpies.

The problem is to know what are the grounds to decide if a bond dissociation enthalpy can be ‘transferred’ from one molecule to another. The most obvious guideline would be based on bond lengths. For a chemical bond involving the same atoms, its length and its strength vary in opposite directions. This has been known for many years and it is illustrated in textbooks, for instance with single, double, and triple carbon-carbon bonds [11]. But how is a bond strength evaluated? In the case of diatomic molecules, it looks simple: the bond strength can be ascribed to the bond dissociation enthalpy. In polyatomic molecules, however, this cannot be done. We can imagine, for example, that the cleavage of a $R-H$ bond (where $R$ is a polyatomic group) is the result of two steps. In the first step the bond is cleaved but the fragments retain the structural and electronic configuration of the parent molecule; this will be followed, in the second step, by the relaxation of the fragments to their ground state. With this procedure we are considering that a bond dissociation enthalpy (the net process) contains some contribution that is **extrinsic** to the $R-H$ bond strength, which is due to the reorganization of the fragment species. The ‘**intrinsic**’ bond strength, which we call $E_s(R-H)$, will therefore be given by the $R-H$ bond dissociation enthalpy less the reorganization energies ($E_R$) of the fragments. To calculate $E_s(R-H)$, also called bond-snap enthalpies, we need values of the reorganization energies, which, of course, are not experimentally available, but can be estimated at $T = 298.15$ K through computational methods.

**Laidler terms**

The so-called Laidler scheme has been developed as a tool to estimate standard enthalpies of formation of organic compounds [12]. It relies on the bond-additivity concept, i.e. it assumes that the **standard enthalpy of atomization** of a given molecule in the gas phase ($\Delta_a H^\circ$, defined as the standard enthalpy of the reaction where all the chemical bonds are cleaved, yielding the gaseous atoms) can be evaluated by adding the relevant bond enthalpy terms.
The best Laidler terms available in the literature are probably those recommended by Cox and Pilcher [13]. They rely on a consistent database including experimentally derived standard enthalpies of formation for hundreds of organic compounds.

2. Gas Phase Ion Energetics

The experimental methods designed to investigate the energetics of gas phase ions have been an important source of thermochemical data, particularly throughout the last two or three decades. Their description, together with some application examples, will be addressed later. Here we shall summarise the main quantities that are measured experimentally and lead to reaction enthalpy values.

**Ionization energy and electron affinity**

The *adiabatic ionization energy* of any molecule AB (mono-, di-, or polyatomic), represented by \( E_i(AB) \), is the *minimum* energy required to remove an electron from the *isolated* molecule at zero kelvin:

\[
AB(g) \rightarrow AB^+(g) + e^-(g) \tag{17}
\]

The proviso \( T = 0 \text{ K} \) signifies that AB is in its electronic, vibrational, and rotational ground states and that it has no translational energy. The word ‘isolated’ indicates the perfect gas model. The ‘minimum energy’ condition insures that AB\(^+\) is also in its electronic, vibrational, and rotational ground states and that the translational energies of AB\(^+\) and e\(^-\) are both zero; it also indicates that the products in reaction (17) do not interact, *i.e.* they also conform with the perfect gas model.

In short, the adiabatic ionization energy is the standard internal energy or the standard enthalpy of reaction (17), at zero kelvin:

\[
E_i(AB) = \Delta U_0^o = \Delta H_0^o \tag{18}
\]

The second important concept we wish to address is the *adiabatic electron affinity*, \( E_{ea} \). For any molecule AB (mono-, di-, or polyatomic), \( E_{ea}(AB) \) is the *minimum* energy required to remove an electron from the *isolated anion* at zero kelvin. In other words, \( E_{ea}(AB) \) is the standard enthalpy of reaction (19) at \( T = 0 \text{ K} \).

\[
AB^-(g) \rightarrow AB(g) + e^-(g) \tag{19}
\]

This definition may appear somewhat counter-intuitive, since the word ‘affinity’ suggests that we should be referring to the reverse process. That is why \( E_{ea} \) is often given as *minus* the enthalpy of reaction (20) at \( T = 0 \text{ K} \) [14]. The definitions are, of course, equivalent, and insure that, in most cases, electron affinities will have positive values.
\[ AB(g) + e^-(g) \rightarrow AB^-(g) \quad (20) \]

**Appearance energy**

Consider a di- or a polyatomic molecule AB in the gas phase, at \( T = 0 \) K. By means of an electron or a photon, this molecule can be ionized and excited to a state \( AB^{*+} \), which subsequently decomposes into the fragments \( A^+ \) and B:

\[ AB(g) \rightarrow AB^{*+}(g) + e^-(g) \rightarrow A^+(g) + B(g) + e^-(g) \quad (21) \]

If \( A^+ \) and B are formed in their ground states and if these species and \( e^- \) have zero translational energies, then the standard enthalpy of reaction (21) at \( T = 0 \) K is equal to the *appearance energy* of \( A^+ \) at \( T = 0 \) K, \( \Delta H^\circ_{\text{A}}(A^+, 0 \) K). It becomes obvious from this definition that, when reporting a value for an appearance energy, it is essential to state the parent molecule. Otherwise, we cannot identify the remaining species in the net reaction (21).

The *appearance energy* (formerly known as *appearance potential*) is a widely used concept in *threshold* mass spectrometry experiments, which involve measuring the minimum energy required to cause a certain process.

**Proton affinity, basicity, and acidity**

In addition to the concepts reviewed before (appearance energy, ionization energy, and electron affinity), three other are relevant in gas phase molecular energetics, namely, *proton affinity*, *gas phase basicity*, and *gas phase acidity*.

The *proton affinity* of any species A in the gas phase, abbreviated by \( E_{\text{pa}}(A) \), is defined as minus the standard enthalpy of reaction (22) at \( T = 298.15 \) K. The minus sign insures that proton affinities have positive values.

\[ A(g) + H^+(g) \rightarrow AH^+(g) \quad (22) \]

The *gas phase basicity* of A, which we will represent by \( \Delta_{\text{base}} G^\circ(A) \), is the standard Gibbs energy of reaction (22). It is also usually defined at \( T = 298.15 \) K and it is related to \( E_{\text{pa}}(A) \) by equation (23).

\[ \Delta_{\text{base}} G^\circ(A) = -E_{\text{pa}}(A) - T\left[ S^\circ(AH^+, g) - S^\circ(A, g) - S^\circ(H^+, g) \right] \quad (23) \]

Finally, the *gas phase acidity* of the molecule AH, represented by \( \Delta_{\text{acid}} G^\circ(AH) \), is the standard Gibbs energy of reaction (24), usually at \( T = 298.15 \) K.

\[ AH(g) \rightarrow A^-(g) + H^+(g) \quad (24) \]

Note that the standard enthalpy of this reaction, \( \Delta_{\text{acid}} H^\circ(AH) \), is equal to the proton affinity of the anion, \( E_{\text{pa}}(A^-) \). This quantity can be related to \( E_{\text{pa}}(A) \) by using the adiabatic ionization energy of AH and the adiabatic electron affinity of A [6].
PART II  Experimental Methods to Derive Bond Energy Data. A Schematic Overview

The methods to derive bond energy data, by alphabetical order, are summarized in Table 1.

Table 1  Experimental methods addressed in Part II.

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<td>Single-Pulse Shock Tubes (SPST)</td>
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<td></td>
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</tr>
</tbody>
</table>

1. BIRGE-SPONER EXTRAPOLATION (BS) [15,16]

Measured quantities  Spacing of vibrational energy levels.
Primary quantities derived  Bond dissociation enthalpies at $T = 0$ K.
Secondary quantities derived  Bond dissociation enthalpies at $T = 298.15$ K.
Application  Diatomic molecules in the gas phase.
Examples/Comments

(1) The linear extrapolation of the vibrational energy levels spacing ($\Delta \varepsilon$) of a diatomic molecule $XY$ to $\Delta \varepsilon = 0$ leads to the vibrational quantum number ($v$) corresponding to the bond dissociation. The procedure relies on the linear anharmonic oscillator model:

$$
\varepsilon = \left(v + \frac{1}{2}\right) \hbar \nu - \left(v + \frac{1}{2}\right)^2 \chi \hbar \nu + \cdots
$$
where $x_e$ is the anharmonicity constant and $v$ is the frequency. When $\Delta \varepsilon = \varepsilon (v+1) - \varepsilon (v) = \varepsilon (v) - \varepsilon (v-1) = 0$ it can be shown that the average value of $v$ is given by

$$v = \frac{1-x_e}{2x_e}$$

and therefore

$$D_H^o (X - Y, 0 K) = \varepsilon \left(1 + \frac{1-x_e}{2x_e}\right) - \varepsilon (v = 0) = \frac{(x_e-1)^2}{4x_e} \nu$$

If the molar heat capacities at constant pressure of all the species involved are known between $T = 0$ and $T = 298.15$ K, the bond dissociation enthalpy at $T = 298.15$ K can be calculated:

$$XY(g) \rightarrow X(g) + Y(g)$$

$$D_H^o (X - Y) = D_H^o (X - Y, 0 K) + \int_0^{298} \Delta C_p dT$$

(2) The linear Birge-Sponer extrapolation usually yields an upper limit of the true bond dissociation enthalpy because higher order terms in the expansion of $\varepsilon$ vs. $v$ are ignored. As a result, the dissociation quantum number, as calculated above, is often higher than the true value.

2. COMBUSTION CALORIMETRY (CC) [13,17-20]

Measured quantities
- Temperature vs. time or heat flux.

Primary quantities derived
- Energies of combustion reactions.

Secondary quantities derived
- Bond dissociation enthalpies. Mean bond dissociation enthalpies.

Application
- Long-lived species.

Examples/Comments
(1) In most combustion calorimetry experiments the reaction between the sample and oxygen or fluorine is investigated and the internal energy change is determined from temperature vs. time plots. One of the main difficulties of these experiments is to insure well defined reaction products. For many substances this can only be achieved by rotating the bomb after the combustion. In this method (Rotating-Bomb Combustion Calorimetry, CC-RB), the combustion products are dissolved in a solution previously placed into the bomb, so that the final composition can be accurately determined. The non-rotating set-up is usually known as Static Bomb Combustion Calorimetry (CC-SB).

(2) The standard molar enthalpy of formation of $MX_n$ in the condensed state is determined by combustion calorimetry and used together with the standard molar enthalpy of vaporization to derive the standard molar enthalpy of formation in the gas phase. If the standard molar enthalpies
of formation of the gaseous species $\text{MX}_{n-1}$ and $\text{X}$ are available, the first $\text{M}−\text{X}$ bond dissociation enthalpy can be calculated:

$$\text{MX}_n(\text{g}) \rightarrow \text{MX}_{n-1}(\text{g}) + \text{X}(\text{g})$$

$$\Delta_i H^o = \Delta_i H^o (\text{MX}_{n-1}, \text{g}) + \Delta_i H^o (\text{X}, \text{g}) - \Delta_i H^o (\text{MX}_n, \text{g}) = D^o_{li}(\text{M}−\text{X})$$

(3) Same situation of the previous example, but only the standard molar enthalpies of formation of the gaseous species $\text{M}$ and $\text{X}$ are available. The mean $\text{M}–\text{X}$ bond dissociation enthalpy, $\langle D^o_{li} \rangle (\text{M}–\text{X})$, can be derived:

$$\text{MX}_n(\text{g}) \rightarrow \text{M}(\text{g}) + n\text{X}(\text{g})$$

$$\Delta_i H^o = \Delta_i H^o (\text{M}, \text{g}) + n\Delta_i H^o (\text{X}, \text{g}) - \Delta_i H^o (\text{MX}_n, \text{g}) = n\langle D^o_{li} \rangle (\text{M}–\text{X})$$

3. DIFFERENTIAL SCANNING CALORIMETRY (DSC) [21]

**Measured quantities**
Differential heat input ($dH/dt$) vs. temperature or time.

**Primary quantities derived**
Enthalpies of reaction and phase transition, heat capacities.

**Secondary quantities derived**
Bond dissociation enthalpies. Mean bond dissociation enthalpies.

**Application**
Solid or liquid long-lived species.

**Examples/Comments**
(1) Whenever a material undergoes a change in physical state or reacts chemically, heat is either absorbed or liberated. Many such processes can be initiated simply by raising the temperature of the material. Modern differential scanning calorimeters are designed to determine the enthalpies of these processes by measuring the differential heat flow required to maintain a sample of the material and an inert reference at the same temperature. This temperature is programmed to scan a temperature range by increasing it linearly at a predetermined rate.

(2) DSC is well suited to study the thermochemistry of reactions where a crystalline sample (e.g. a transition metal complex) decomposes, with loss of a gaseous ligand:

$$\text{ML}_n\text{X}_m(\text{cr}) = \text{MX}_m(\text{cr}) + n\text{L}(\text{g})$$

If the enthalpy of this decomposition reaction ($\Delta_{\text{dec}} H^o$) can be referred to the gas phase (by using the enthalpies of sublimation of the two crystalline compounds), then it is identified with the mean $\text{M}–\text{L}$ bond dissociation enthalpy:

$$n\langle D^o_{li} \rangle (\text{M}–\text{L}) = \Delta_{\text{dec}} H^o + \Delta_{\text{sub}} H^o (\text{MX}_m) - \Delta_{\text{sub}} H^o (\text{ML}_n\text{X}_m)$$

(3) It is important to notice that the measured $\Delta_{\text{dec}} H^o$ values usually refer to temperatures well above $T = 298.15$ K. The temperature correction requires heat capacity data for $\text{ML}_n\text{X}_m$, $\text{MX}_m$, and $\text{L}$.

(4) DSC has also been used to study other types of reaction such as ligand replacements and isomerizations.
4. ELECTROCHEMICAL MEASUREMENTS (EChem) [22-27]

**Measured quantities**  
Reversible redox potentials.

**Primary quantities derived**  
Gibbs energies of reaction in solution.

**Secondary quantities derived**  
Bond dissociation Gibbs energies in solution. Bond dissociation enthalpies.

**Application**  
Species in solution.

**Examples/Comments**

(1) Techniques such as cyclic voltammetry and photomodulation voltammetry have been used to measure redox potentials.

(2) The following scheme leads to the R–H bond dissociation Gibbs energy (NHE stands for ‘normal hydrogen electrode’):

\[
\begin{align*}
\text{RH(sln)} &= \text{R}^-\text{(sln)} + \text{H}^+(\text{sln}) \\
\text{R}^-\text{(sln)} &= \text{R(}\text{sln}) + e^- \\
\text{H}^+(\text{sln}) + e^- &= \text{H(}\text{sln}) \\
\text{Net: } \text{RH(sln)} &= \text{R(}\text{sln}) + \text{H(}\text{sln})
\end{align*}
\]

\[
\Delta_rG = 2.303RTpK_{\text{RH}}
\]

\[
\Delta_rG = F_{\text{NHE(}aq)}^{\circ}\left(\text{R/R}^--\right)_S
\]

\[
\Delta_rG = -F_{\text{NHE(}aq)}^{\circ}\left(H^+/H\right)_S
\]

\[
D_{G_{\text{sln}}(\text{R–H})} = 2.303RTpK_{\text{RH}} + F_{\text{NHE(}aq)}^{\circ}\left(\text{R/R}^--\right)_S - F_{\text{NHE(}aq)}^{\circ}\left(H^+/H\right)_S
\]

The application of this equation requires an estimate of the reduction potential of H$^+$ in the same solvent where the experiments were carried out. $E_{\text{NHE(}aq)}^{\circ}\left(H^+/H\right)_S$ depends on thermodynamic parameters of the gaseous hydrogen atom (the Gibbs energy of formation and the Gibbs energy of solvation in the solvent S) and of the proton (the Gibbs energy of transfer from S to water):

\[
- FE_{\text{NHE(}aq)}^{\circ}\left(H^+/H\right)_S = \Delta_rG^{\circ}(H,g) + \Delta_{\text{sln}}G(H,g) + \Delta_{\text{transf}}G(H^+,S\to aq)
\]

Once $D_{G_{\text{sln}}(\text{R–H})}$ is known, the R–H bond dissociation enthalpy in the solvent S can be derived through the equation below. The calculation requires, however, an estimate for the solvation entropies of H, R and RH. It is often assumed that the solvation entropies of the latter two species are identical.

\[
D_{H_{\text{sln}}}(\text{R–H}) = D_{G_{\text{sln}}(\text{R–H})} + T\left[S^{\circ}(H,g) + S^{\circ}(R,g) - S^{\circ}(\text{RH},g)\right]
\]

\[
+ T\left[\Delta_{\text{sln}}S(H,g) + \Delta_{\text{sln}}S(R,g) - \Delta_{\text{sln}}S(\text{RH},g)\right]
\]

Finally, the R–H bond dissociation enthalpy in the gas-phase can be obtained from the following equation, which includes the solvation enthalpies of RH and R.

\[
D_{H}^{\circ}(\text{R–H}) = 2.303RTpK_{\text{RH}} + F_{\text{NHE(}aq)}^{\circ}\left(\text{R/R}^--\right)_S + \Delta_{\text{transf}}G(H^+,S\to aq) + \Delta_rH^{\circ}(H,g)
\]

\[
+ 0.5TS^{\circ}(H_2,g) + T\left[S^{\circ}(R,g) - S^{\circ}(\text{RH},g)\right] + T\left[\Delta_{\text{sln}}S(R,g) - \Delta_{\text{sln}}S(\text{RH},g)\right]
\]

\[
+ \Delta_{\text{sln}}H(\text{RH},g) - \Delta_{\text{sln}}H(R,g)
\]
(3) The previous equation can be simplified by cancelling the solvation entropies and enthalpies of R and RH. Although this is not always a good assumption, it is frequently used in the literature. Moreover, it is usual to combine most of the terms of last equation in a single constant, C, which is empirically adjusted to give better agreement with gas phase data. For instance, the equation below \( (C = 306.7 \text{ kJ mol}^{-1}) \) illustrates this procedure for \( S = \text{dimethylsulphoxide} \) and when the oxidation potential of \( R^- \) is referred to the ferrocene/ferrocenium (Fc/Fc\(^+\)) couple instead of the NHE in water.

\[
D_H^o(R-H) = 2.303RTpK_{RH} + FE^o_{Fe/Fe^+}(R/R^-)_{DMSO} + 306.7 \text{ kJ mol}^{-1}
\]

(4) The p\(K_a\) is another experimental value required. It can be obtained by equilibrium methods in solution (e.g. IR spectroscopic measurements of proton transfer equilibria).

(5) Many assumptions related to the methodology described above are avoided if relative values of bond dissociation Gibbs energies or enthalpies are derived, for example, \( D_{Gss}^o(X-H) - D_{Gss}^o(Y-H) \) or \( D_{Gss}^o(X-H) - D_{Gss}^o(Y-H) \). These data should rely on redox potentials and p\(K_a\) values measured in the same solvent and using the same electrolyte, leading to the cancellation of the constant C.

(6) Bond dissociation Gibbs energies such as \( D_{Gss}^o(X-H) \) and \( D_{Gss}^o(X-H) \), identified with the Gibbs energies of the reactions

\[
\begin{align*}
RH^+(sln) &= R(sln) + H^+(sln) \\
RH^-(sln) &= R^-(sln) + H(sln)
\end{align*}
\]

can also be obtained by measuring the redox potentials of RH.

(7) Redox potentials have also been determined through equilibrium studies in solution, e.g. using pulse radiolysis to generate \( X \) from a suitable precursor:

\[
X(sln) + Y^-(sln) = X^-(sln) + Y(sln)
\]

5. \textbf{ELECTRON IMPACT MASS SPECTROMETRY (EIMS) [28,29]}

\textit{Measured quantities} \quad \text{Ion intensities vs. electron energy.}

\textit{Primary quantities derived} \quad \text{Appearance energies.}

\textit{Secondary quantities derived} \quad \text{Enthalpies of reaction. Bond dissociation enthalpies.}

\textit{Application} \quad \text{Species in the gas phase.}

\textit{Examples/Comments}

(1) The method is similar to that described for Photoionization Mass Spectrometry, i.e. it relies on appearance energy measurements. Electron impact has, however, less favourable threshold ionization probability than photon impact. Also, only very few EIMS studies reported in the literature used a monoenergetic electron beam.

(2) Provided that there is no reverse activation barrier and in the absence of a kinetic shift (see Photoionization Mass Spectrometry), there is experimental evidence that the appearance energy of \( A^+ \), \( A_0(A^+) \), measured by electron impact,
AB(g) + e\(^-\) → A\(^+(g)\) + B(g) + 2e\(^-\)

can be related to the A–B bond dissociation enthalpy at \(T = 298.15\) K without any further correction. \(E_i(A)\) is the adiabatic ionization energy of A.

\[ D_{H}^{\circ}(A - B) = A_{E}(A^{+}) - E_{i}(A) \]

The same applies to the standard enthalpy of formation of A\(^+\) or B:

\[ \Delta_{f}^{\circ}H(A^{+}, g) = A_{E}(A^{+}) - \Delta_{f}^{\circ}H(B, g) + \Delta_{f}^{\circ}H(AB, g) \]
6. ELECTRON PHOTODETACHMENT SPECTROSCOPY (EPDS) [30-32]

**Measured quantities**
Ion intensities vs. photon energy.

**Primary quantities derived**
Electron affinities.

**Secondary quantities derived**
Enthalpies of reaction. Bond dissociation enthalpies.

**Application**
Species in the gas phase.

**Examples/Comments**

1. In EPDS of negative ions the disappearance of $A^-$, due to the process

$$A^-(g) \rightarrow h\nu A(g) + e^-$$

is monitored as a function of the photon energy. The anions may be trapped in the cell of an ion cyclotron resonance mass spectrometer and their signal intensity is measured with and without irradiation and converted to the photodetachment cross section. This cross section vs. the radiation wavelength is the photodetachment spectrum. The threshold is determined by fitting the experimental data with theoretical models.

2. Flowing Afterglow-Selected Ion Flow Tube is another type of mass spectrometry that has been used for EPDS experiments.

3. Electron affinities can be coupled, for instance, with acidities, and yield bond dissociation enthalpies. See Flowing Afterglow-Selected Ion Flow Tube.

7. EQUILIBRIUM IN THE GAS PHASE (EG) [33-35]

**Measured quantities**
Equilibrium concentrations at one or several temperatures.

**Primary quantities derived**
Equilibrium constants. Gibbs energies and enthalpies of reaction.

**Secondary quantities derived**
Bond dissociation enthalpies. Mean bond dissociation enthalpies.

**Application**
Species in the gas phase.

**Examples/Comments**

1. Van't Hoff plots lead to enthalpies of reactions in the gas phase, from which bond dissociation enthalpies can be derived. For example:

$$MX_n(g) + AB(g) = MX_{n-1}A(g) + XB(g)$$

$$\Delta_T H^o = D^o_H(M - X, T) + D^o_H(A - B, T) - D^o_H(M - A, T) - D^o_H(X - B, T)$$

2. In the case of equilibria involving ionic species, other quantities have to be known in order to derive homolytic bond dissociation enthalpies. The enthalpy of the reaction

$$XH^+(g) + Y(g) = YH^+(g) + X(g)$$

equals the difference between the proton affinities of $X$ and $Y$, which is equivalent to a bond dissociation enthalpy difference:
\[ \Delta_i H_m^o = E_{pa}(X) - E_{pa}(Y) = D_{H^+}^o(X-H^+) - D_{H^+}^o(Y-H^+) \]

The proton affinity of X can be obtained if \( E_{pa}(Y) \) is known. The bond dissociation enthalpy \( D_{H^+}^o(X-H^+) \) can be used to derive \( D_{H^+}^o(X^+ - H) \) if the adiabatic ionization energy of X, \( E_i(X) \), is available:

\[ D_{H^+}^o(X^+ - H) = D_{H^+}^o(X-H^+) + E_i(X) - E_i(H) \]

Finally, the X–H bond dissociation enthalpy for the neutral species, XH, can be calculated if the adiabatic ionization energy of XH is known:

\[ D_{H^+}^o(X-H) = D_{H^+}^o(X-H^+) + E_i(XH) - E_i(H) \]

(3) For other examples see, e.g., Ion Cyclotron Resonance Mass Spectrometry and Flowing Afterglow-Selected Ion-Flow Tube.

(4) The temperature to which a reaction enthalpy refers is taken as the mean value of the temperature interval used in the van't Hoff plot (this is known as the Second Law treatment of experimental data). The reaction enthalpy can be corrected to \( T = 298.15 \) K when the relevant heat capacity values are available.

(5) For some reactions the equilibrium constant is known at only one temperature. This may lead to bond dissociation Gibbs energies or even to bond dissociation enthalpies if the reaction entropies can be estimated (this is called the Third Law method).

8. EQUILIBRIUM IN SOLUTION (ES) [13,33,36]

**Measured quantities**

Equilibrium concentrations at one or several temperatures.

**Primary quantities derived**

Equilibrium constants. Gibbs energies and enthalpies of reaction in solution.

**Secondary quantities derived**

Bond dissociation enthalpies. Mean bond dissociation enthalpies.

**Application**

Species in solution.

**Examples/Comments**

(1) If equilibrium constants are available at several temperatures, van't Hoff plots lead to enthalpies of reaction in solution, from which bond dissociation enthalpies can be derived (see examples in Reaction Solution Calorimetry).

(2) Virtually every instrumental technique that affords concentrations of the species in equilibrium, such as FT-IR, UV-Vis spectroscopy, EPR, NMR, etc., has been used to study the thermochemistry of reactions in solution.

(3) The temperature to which a reaction enthalpy refers is taken as the mean value of the experimental temperature interval. The reaction enthalpy value is usually not corrected to \( T = 298.15 \) K because the relevant heat capacity data are not available.
(4) For some reactions the equilibrium constant is known at only one temperature. This may lead to bond dissociation Gibbs energies or even to bond dissociation enthalpies if the reaction entropies can be estimated.
9. FLOWING AFTERGLOW - SELECTED ION-FLOW TUBE (FA-SIFT) [37-41]

Measured quantities
Ion intensities. Ion intensities vs. time. Ion intensities vs. ion kinetic energy.

Primary quantities derived
Equilibrium constants. Rate constants.

Secondary quantities derived
Enthalpies of reaction. Bond dissociation enthalpies.

Application
Species in the gas phase.

Examples/Comments
(1) The equilibrium constant for the reaction

\[ \text{XH}(g) + \text{Y}^-(g) = \text{YH}(g) + \text{X}^-(g) \]

can be determined at one or several temperatures, usually by measuring the forward and the reverse rate constants. In either case it is possible to evaluate the enthalpy of reaction, from a van't Hoff plot or by calculating the entropies of reactants and products. The enthalpy of reaction can be expressed in terms of the acidities of XH and YH:

\[ \Delta_H^o = D_H^o (\text{X}^- - \text{H}^+) - D_H^o (\text{Y}^- - \text{H}^+) \]

The acidity of XH, which can be obtained if the acidity of YH is known, is used to calculate the bond dissociation enthalpy \( D_H^o (\text{X}^- - \text{H}^+) \) by taking the adiabatic electron affinity of X and the ionization energy of the hydrogen atom:

\[ D_H^o (\text{X}^- - \text{H}^+) = D_H^o (\text{X}^- - \text{H}^+) + E_{ia}(\text{X}) - E_i(\text{H}) \]

(2) Ion-molecule reactions usually occur with very small activation energies, implying that when such a reaction is observed in the gas phase, its enthalpy will be less than ca. 10 kJ mol\(^{-1}\). This affords a method (the so-called bracketing method) to determine limits for bond dissociation enthalpies. For example, if the reaction given above is observed for Y\(^-\) and not observed for a reactant Z\(^-\), then \( D_H^o (\text{Y}^- - \text{H}^+) \geq D_H^o (\text{X}^- - \text{H}^+) \geq D_H^o (\text{Z}^- - \text{H}^+) \).

10. GUIDED ION BEAM MASS SPECTROMETRY (GIBMS) [42,43]

Measured quantities
Ion intensities vs. ion kinetic energy.

Primary quantities derived
Reaction cross sections.

Secondary quantities derived
Enthalpies of reaction. Bond dissociation enthalpies.

Application
Species in the gas phase.

Examples/Comments
(1) Thermochemical information at \( T = 0 \) K for the endothermic reaction (M is an atom)

\[ \text{M}^+(g) + \text{AB}(g) \rightarrow \text{MB}^+(g) + \text{A}(g) \]

can be obtained from the threshold energy \( (E_0) \), by assuming that there are no activation barriers in excess of the positive enthalpy of the reaction:

\[ D_H^o (\text{M}^+ - \text{B}, 0 \text{ K}) = D_H^o (\text{A} - \text{B}, 0 \text{ K}) - E_0 \]
$E_0$ is calculated by using an empirical model to fit the experimental variation of the reaction cross section with the kinetic energy of $M^+$:

$$\sigma(E) = \sigma_0 \sum g_i (E + E_i - E_0)^n / E$$

where $E$ is the relative kinetic energy, $\sigma_0$ is an energy-independent scaling factor, and $n$ is an adjustable parameter. The sum is over the distribution of electronic, vibrational and rotational reactant states $i$, with energies $E_i$ and relative populations $g_i$. This model is then convoluted with the kinetic energy distribution of the reactants before comparison to the data. The parameters $\sigma_0$, $n$, and $E_0$ are optimized by using a non-linear least squares analysis.

(2) The threshold of the reaction

$$M^+(g) + AB(g) \rightarrow MB(g) + A^+(g)$$

affords the bond dissociation enthalpy in the neutral species MB.

(3) Collision-induced dissociation (CID) is another methodology to derive bond enthalpy data from GIBMS experiments. The ion of interest can be accelerated to a given energy to decompose upon collision with a neutral species (e.g. an xenon atom):

$$MB^+(g) + Xe(g) \rightarrow M^+(g) + B(g) + Xe(g)$$

The threshold for the formation of $M^+$ can be identified with the $M^+$–B bond dissociation enthalpy at $T = 0$ K after analyzing the data using the model noted above.

(4) The bond dissociation enthalpies at $T = 298.15$ K can be calculated if the relevant molar heat capacities are available.

11. HIGH PRESSURE MASS SPECTROMETRY (HPMS) [44-47]

**Measured quantities**

Ion intensities at one or several temperatures.

**Primary quantities derived**

Equilibrium constants.

**Secondary quantities derived**

Gibbs energies and enthalpies of reaction. Bond dissociation enthalpies.

**Application**

Species in the gas phase.

**Examples/Comments**

Reaction equilibria involving ion-molecule reactions can be studied by HPMS. This technique differs from Pulsed High Pressure Mass Spectrometry because here the reactant ions are not produced in the collision cell. These ions (e.g. metal ions) are formed, e.g. by electron impact or by surface ionization of a suitable precursor, accelerated, mass selected, decelerated, and injected in a reaction cell containing the neutral reactant. The ions are thermallized by several collisions with the reactant gas and ion-molecule reaction equilibrium is established. The measurement of equilibrium constants at one or several temperatures leads to Gibbs energies or to enthalpies of reaction. For example, the enthalpy of the reaction

$$MX_{n-1}^+(g) + X(g) = MX_n^+(g)$$
obtained from a van't Hoff plot, is equal to $-D_h^o(X_{m+1}^+ - X)$.

12. ION CYCLOTRON RESONANCE MASS SPECTROMETRY (ICR) [48-52]

**Measured quantities**
- Ion intensities.
- Ion intensities vs. time.
- Ion intensities vs. electron or photon energy.

**Primary quantities derived**
- Equilibrium constants.
- Rate constants.

**Secondary quantities derived**
- Gibbs energies and enthalpies of reaction.
- Bond dissociation enthalpies.

**Application**
- Species in the gas phase.

**Examples/Comments**

1. Bond enthalpy data can be extracted from equilibrium ICR studies involving either negative or positive ions. An example for the latter is given under Equilibrium in the Gas Phase. For equilibria involving negative ions the enthalpy of the reaction

$$XH^- (g) + Y(g) = YH^- (g) + X(g)$$

equals the difference between the hydride affinity ($H_A$) of X and Y, which is equivalent to a bond dissociation enthalpy difference:

$$\Delta H^o = H_A(X) - H_A(Y) = D_h^o(X-H^-) - D_h^o(Y-H^-)$$

The hydride affinity of X can be obtained if $H_A(Y)$ is known. The bond dissociation enthalpy $D_h^o(X-H^-)$ can be used to derive $D_h^o(X-H)$ if the adiabatic electron affinity of X, $E_{ca}(X)$, is available:

$$D_h^o(X-H^-) = D_h^o(X-H) - E_{ca}(X) + E_{ca}(H)$$

Finally, the X–H bond dissociation enthalpy for the neutral species, XH, can be calculated if the adiabatic electron affinity of XH is known:

$$D_h^o(X-H) = D_h^o(X-H^-) - E_{ca}(XH) + E_{ca}(H)$$

2. Gas phase acidities can also be determined from ICR experiments (see Flowing Afterglow-Selected Ion Flow Tube and Pulsed High Pressure Mass Spectrometry).

3. Ion-molecule reactions usually occur with very small activation energies, implying that when such a reaction is observed in the gas phase, its enthalpy will be less than ca. 10 kJ mol$^{-1}$. This affords a method (the so-called bracketing method) to determine limits for bond dissociation enthalpies. For example, if the reaction given above is observed for Y and not observed for a reactant Z, then $H_A(Y) \geq H_A(X) \geq H_A(Z)$.

4. Collision-induced dissociation (CID) is another methodology to derive bond enthalpy data from ICR experiments. The ion of interest can be accelerated to a given translational energy in the ICR cell and decomposed upon collision with a neutral species (e.g. an argon atom):

$$AXB^+(g) + Ar(g) \rightarrow AX^+(g) + B(g) + Ar(g)$$
The threshold for the formation of AX\(^+\) can be identified with the AX\(^+\)–B bond dissociation enthalpy if both AXB\(^+\) and AX\(^+\) are in their ground states. Competeive CID experiments, providing limits to bond dissociation enthalpies, can also be made:

\[
\text{AXB}^+(g) + \text{Ar}(g) \rightarrow \text{AX}^+(g) + \text{B}(g) + \text{Ar}(g)
\]

\[
\text{AXB}^+(g) + \text{Ar}(g) \rightarrow \text{BX}^+(g) + \text{A}(g) + \text{Ar}(g)
\]

If the signal intensity for AX\(^+\) is larger than for BX\(^+\), then \(D_H^o(\text{BX}^+ - \text{A}) > D_H^o(\text{AX}^+ - \text{B})\).

Photodissociation experiments in ICR cells have also been used to derive bond dissociation enthalpies in ionic species (see Photoionization Mass Spectrometry).

Ionization and electron attachment Gibbs energies can be obtained from ICR equilibrium (see Pulsed High Pressure Mass Spectrometry) or bracketing experiments. Equilibria are usually studied at a single temperature, but entropies can be estimated to derive the enthalpy changes associated with those processes.

It is usually assumed that ICR results refer to \(T = 298.15\) K.

13. KINETIC ENERGY RELEASE DISTRIBUTIONS (KERD) [53]

**Measured quantities**
Ion intensities vs. product kinetic energy.

**Primary quantities derived**
Enthalpies of reaction. Bond dissociation enthalpies.

**Secondary quantities derived**
Species in the gas phase.

**Examples/Comments**

(1) While ion beam experiments are useful for probing the energetics of endothermic reactions (see Guided Ion Beam Mass Spectrometry), they are unable to provide that information for exothermic reactions that occur without activation energies. In these cases, the KERD method may be used to derive thermochemical data. The excess internal energy of a given product, which, for instance is extracted from a high pressure ion source (see High Pressure Mass Spectrometry), may be enough to yield molecular rearrangements or decomposition. If this process occurs in a field-free region of, e.g. a reverse geometry double focusing mass spectrometer (i.e. between the magnetic and the electric sectors), its metastable peak can be recorded and differentiated to yield the kinetic energy release distribution of the decomposition product.

(2) For example, the species \((\text{MX}_n)^+\)* was formed with internal excess energy by an exothermic reaction. Its decomposition in the field-free region,

\[
(\text{MX}_n)^+(g) \rightarrow \text{MX}_{n-1}^+(g) + \text{X}(g)
\]

may lead to the M\(^+\)–X bond dissociation enthalpy at \(T = 0\) K by using phase space theory to fit the product kinetic energy release distribution.

14. KINETICS IN THE GAS PHASE (KG) [54-57]
Measured quantities
Concentrations vs. time at several temperatures.

Primary quantities derived
Rate constants. Enthalpies of activation.

Secondary quantities derived
Enthalpies of reaction. Bond dissociation enthalpies.

Application
Species in the gas phase.

Examples/Comments
1) The enthalpy of activation of a reaction can be derived from an Eyring plot, i.e. a plot of \( \ln\left(\frac{k}{T^n}\right) vs. \frac{1}{T} \) (\( k \) is a rate constant). If a similar plot is obtained for the reverse reaction, the difference between the forward and the reverse enthalpies of activation equals the enthalpy of the reaction, from which bond dissociation enthalpies can be derived (see, e.g. the first example under Reaction Solution Calorimetry with all the species in the gas phase).

2) Often the enthalpy of activation for the reverse reaction is unknown and must be estimated.

3) See also Laser-Powered Homogeneous Pyrolysis, Very Low Pressure Pyrolysis, and Single-Pulse Shock Tubes.

4) The temperature to which a reaction enthalpy refers is taken as the mean value of the experimental temperature interval. The reaction enthalpy value may be corrected to \( T = 298.15 \) K if the relevant heat capacity data are available.

15. KINETICS IN SOLUTION (KS) [33,36,58]

Measured quantities
Concentrations vs. time at several temperatures.

Primary quantities derived
Rate constants. Enthalpies of activation in solution.

Secondary quantities derived
Enthalpies of reaction in solution. Bond dissociation enthalpies.

Application
Species in solution.

Examples/Comments
1) The enthalpy of activation of a reaction can be derived from an Eyring plot. If a similar plot is obtained for the reverse reaction, the difference between the forward and the reverse enthalpies of activation equals the enthalpy of the reaction, from which bond dissociation enthalpies can be derived (see, e.g. the first example under Reaction Solution Calorimetry).

2) In reactions involving the homolytic cleavage of a bond, the enthalpy of activation for the radical recombination reaction, which usually is not available, is estimated as ca. 10 kJ mol\(^{-1}\) (diffusion-controlled reaction).

3) Virtually every instrumental technique that affords concentrations, such as FT-IR, UV-Vis spectroscopy, EPR, NMR, etc., has been used to study the kinetics of reactions in solution.

4) The temperature to which a reaction enthalpy refers is taken as the mean value of the temperature interval. The reaction enthalpy value is usually not corrected to \( T = 298.15 \) K because the relevant solution heat capacity data are not available.

16. KNUDSEN CELL - MASS SPECTROMETRY (KC-MS) [59-61]
**Measured quantities**
- Ion intensities vs. temperature.

**Primary quantities derived**
- Equilibrium constants. Gibbs energies and enthalpies of reaction.

**Secondary quantities derived**
- Bond dissociation enthalpies.

**Application**
- Neutral species in the gas phase.

**Examples/Comments**
1. This technique is also known as High Temperature Mass Spectrometry.
2. Most experiments involving the combination of a Knudsen cell and a mass spectrometer are made over a high temperature range, i.e. the cell is enclosed in a furnace. The equilibrium partial pressure of any species $i$ ($p_i$) within the cell is determined by monitoring the intensity $I_i$ of its parent ion with the mass spectrometer:

   $p_i = \frac{K_i I_i^+}{A_i} T$

   T is the absolute temperature, $A_i$ is the fractional isotopic abundance of species $i$, and $K_i$ is a calibration constant that depends on the sensitivity of the mass spectrometer and on the nature of $i$. Vapour pressures down to $10^{-7}$ Pa can be measured by this method.

3. An enthalpy of reaction can be derived from the equilibrium constants $K_p$ by a van't Hoff plot (in which case the temperature considered is the average of the experimental temperature interval) or, at a given temperature, by the Third Law method:

   $\Delta G^o_i = \Delta H^o_i - T \Delta S^o_i = -RT \ln K_p(T)$

   This equation transforms into

   $\Delta H^o = -RT \ln K_p(T) - T \sum_i v_i [G^o_i(T) - H^o_i(298)] / T$

   where $v_i$ is the stoichiometric coefficient of species $i$, and $G^o_i(T)$ and $H^o_i(298)$ are the Gibbs energy and the enthalpy, at temperatures $T$ and 298.15 K, respectively. These quantities can be obtained through statistical mechanics calculations or taken from data tables.

4. The Third Law method is usually preferred over the van't Hoff plot: it yields several independent values of $\Delta H^o$ (at $T = 298.15$ K), one for each temperature of measurement. The average value of $\Delta H^o$ is then used to derive the standard molar enthalpy of formation of the species of interest (from which bond enthalpy data can be obtained).

17. LASER-POWERED HOMOGENEOUS PYROLYSIS (LPHP) [62-64]
Examples/Comments

(1) In LPHP experiments the molecule MXₙ is thermally activated by collisions with a bath gas (avoiding the complications in some VLPP experiments, related to catalytic decomposition at the reactor walls). This bath gas is heated by collision with molecules of a substance that absorbs radiation from, e.g. a CO₂-pulsed laser beam. The sudden temperature increase is followed by a rapid cooling due to expansion to the surrounding gas, which quenches the unimolecular reaction:

\[ \text{MX}_n(g) \rightarrow \text{MX}_{n-1}(g) + X(g) \]

The reaction temperature is measured by using an internal standard, i.e. a reaction whose Arrhenius parameters are well known and which has rates similar to the decomposition of MXₙ. The products may be analysed by mass spectrometry. The ratio between the activation energies of the sample decomposition and the standard is obtained from the ratios of the respective rate constants vs. temperature. As the pressure range used in LPHP experiments is considerably higher than that in very low pressure pyrolysis cells, the fall-off correction of the experimental activation energy for the above reaction is smaller than in the case of VLPP.

(2) The high pressure limit of the activation energy, \( E_\infty(T) \), for the above decomposition reaction is usually measured at temperatures well above 298.15 K (\( T \) is the mean of the experimental temperature interval). The enthalpy of reaction at \( T = 298.15 \) K is derived from the equation:

\[
D^\circ_{\text{M-X}}(M-X) = E_\infty(T) - (T-298)\langle \Delta U^\circ_{\text{r-1}} \rangle - T\langle \Delta^{\ddagger}C_v^\circ \rangle - T\langle \Delta^{\ddagger}C_v^\circ \rangle
\]

by assuming that the internal energy of activation (\( \Delta^\ddagger U^\circ_{\text{r-1}} \)) for the reverse reaction at \( T = 0 \) K is zero. The second term includes the average molar heat capacity difference between products and reactants in the 298.15–\( T \) K temperature range, and the last term contains the average molar heat capacity difference between the transition state and the products in the 0–298.15 K temperature range. These heat capacities can be calculated by statistical mechanics or derived from empirical methods.

18. MASS SPECTROMETRY - KINETIC METHOD (MS-K) [65]

Measured quantities

Ion intensities.

Primary quantities derived

Rate constant ratio.

Secondary quantities derived

Enthalpies of reaction. Bond dissociation enthalpies.

Application

Species in the gas phase.

Examples/Comments

(1) The (metastable or collision-induced) decomposition of a proton-bound dimer, X--H⁺--B, yields the ions XH⁺ and BH⁺, with rate constants \( k_1 \) and \( k_2 \), respectively. If this dissociation depends only on the critical energies of the two competitive processes (i.e. ignoring entropic effects) and if there are no significant secondary dissociations, the abundances of XH⁺ and BH⁺ will reflect the relative proton affinities of X and B. It can be shown that
\[ \ln \left( \frac{XH^+}{BH^+} \right) = \left[ E_{pa}(X) - E_{pa}(B) \right] C \]

where \( C \) is a constant. Therefore, by measuring the ratio of the ion abundances for a series of \( X \) with known proton affinities, a plot of the ratio against \( E_{pa}(X) \) affords \( E_{pa}(B) \) as the intercept.

(2) See the example involving proton affinity under Equilibrium in the Gas Phase.

19. PHOTOACOUSTIC CALORIMETRY (PAC) [66-69]

**Measured quantities**
Amplitude of photoacoustic signal and solution transmittance.

**Primary quantities derived**
Enthalpies of reaction in solution.

**Secondary quantities derived**
Bond dissociation enthalpies.

**Application**
Species in solution.

**Examples/Comments**

(1) The chemical or physical processes are initiated by a pulse of radiation. Part of the pulse energy is consumed in the process and the remaining energy is deposited in solution yielding a pressure wave. The amplitude of this wave is proportional to the energy deposited in solution. The overall energy balance equation is

\[ E_o = N_A h \nu = \phi_m E_o + \Phi_f E_f + \Phi_u E_u \]

where \( N_A h \nu \) is the pulse energy, \( \phi_m \) is the "non-radiative quantum yield", evaluated from the experimental data, and the product \( \phi_u E_u \) represents the observed heat deposited in solution; \( \Phi_f E_f \) reflects the energy lost by fluorescence, and \( \Phi_u E_u \) gives the enthalpy associated with the process under study (\( \Delta H^o \) for a chemical reaction).

(2) In order to derive the true value of \( \phi_m \), which is associated with the thermal expansion, it is often necessary to correct the observed non-radiative quantum yield by considering the ‘intrinsic volume change’ of the process under study.

(3) The enthalpy of reaction is measured and identified with the X–Y bond dissociation enthalpy in solution:

\[ \Delta H^o = D_H^o (X - Y) \]

(4) The enthalpy of the net reaction is measured and identified with a balance of several bond dissociation enthalpies in solution (for example, \( A_2 \) is tert-butylperoxide and \( RH \) is phenol):

\[ \Delta H^o = 2D_H^o (R - H) + D_H^o (A - A) - 2D_H^o (A - H) \]
(5) It is often assumed that the solvation enthalpies cancel, so that the bond dissociation enthalpies are close to the gas phase values.

20. PHOTOCALORIMETRY (PC) [70-73]

*Measured quantities*  
Temperature vs. time or heat flux.

*Primary quantities derived*  
Enthalpies of reaction in solution.

*Secondary quantities derived*  
Bond dissociation enthalpies. Mean bond dissociation enthalpies.

*Application*  
Long-lived species.

*Examples/Comments*  
The thermochemistry of radiation-activated reactions can be probed with photocalorimeters. These instruments are normal calorimeters (e.g. isoperibol reaction-solution calorimeters or heat-flux calorimeters) which include an optical system that allows the irradiation of the sample in the calorimetric vessel.

21. PHOTOELECTRON SPECTROSCOPY (PES) [74-77]

*Measured quantities*  
Electron count vs. electron kinetic energy.

*Primary quantities derived*  
Ionization energies. Electron affinities.

*Secondary quantities derived*  
Enthalpies of reaction. Bond dissociation enthalpies.

*Application*  
Species in the gas phase.

*Examples/Comments*  
(1) In photoelectron spectroscopy experiments the minimum energies associated with the processes

\[
\text{A}(g) \rightarrow A^+(g) + e^- \\
\text{A}^-(g) \rightarrow A(g) + e^-
\]

are measured. As the radiation wavelength is fixed, the kinetic energies of the electrons are determined by the energies required to ionize the species A or A^−. A^+ or A are produced in various vibrational and electronic states. If the 0σ−0 vibrational transition is detected, the adiabatic ionization energy or electron affinity can be obtained.

(2) Ionization energies and electron affinities can be coupled with a variety of other quantities (proton affinities, hydride affinities, etc.), to yield bond dissociation enthalpies.

22. PHOTOIONIZATION MASS SPECTROMETRY (PIMS) [14,78-80]

*Measured quantities*  
Ion intensities vs. photon energy.

*Primary quantities derived*  
Appearance energies. Adiabatic ionization energies.
Secondary quantities derived

Enthalpies of reaction. Bond dissociation enthalpies.

Application

Species in the gas phase.

Examples/Comments

(1) Provided that there is no reverse activation barrier and in the absence of a kinetic shift (see below), the A–B bond dissociation enthalpy at \( T = 0 \) K can be obtained from the experimental appearance energy of \( \text{A}^+ \), which is identified with the threshold of the photoionization efficiency curve (ion intensity vs. photon energy). This onset is determined by a linear extrapolation to zero (background level of the signal) of the linear portion of the curve.

\[
\text{AB}(g) \rightarrow \text{A}^+(g) + \text{B}(g) + e^-
\]

\[ D_0^d(A - B, 0 \text{ K}) = A_{E_0}(A^+, 0 \text{ K}) - E_i(A) + \langle E_i \rangle \]

\( \langle E_i \rangle \) is the sum of the average vibrational and rotational energies of AB (at the experimental temperature) effective in dissociation and \( E_i \) is the adiabatic ionization energy of A (known, e.g., from UV photoelectron experiments).

(2) The A–B bond dissociation enthalpy can also be derived if the adiabatic ionization energy of AB is available:

\[ D_0^a(A^+ - B, 0 \text{ K}) = A_{E_0}(A^+, 0 \text{ K}) - E_i(\text{AB}) + \langle E_i \rangle \]

(3) If \( \langle E_i \rangle \) is not considered, the obtained bond dissociation enthalpies will be lower limits of the true values. However, an opposite effect may be caused by the fact that dissociation at a finite rate, determined by the time scale for ion detection, requires ‘internal’ energy in excess for threshold. This is the so-called kinetic shift and implies that the experimental \( A_{E_0}(\text{A}^+) \) is an upper limit of the true value. The possible cancellation of the two effects justifies the assumption in some PIMS experiments that the data \( (A_{E_0} \text{ and } E_i) \) lead directly to bond dissociation enthalpies at \( T = 298.15 \) K (see below for a more accurate treatment of data).

(4) The internal energy of the ion is more precisely defined in experiments where the ions are detected in coincidence with energy-selected electrons (PEPICO).

(5) The bond dissociation enthalpies at \( T = 298.15 \) K can be calculated if the relevant molar heat capacities are available.

(6) The calculation of standard enthalpies of formation of the ionic species at \( T = 298.15 \) K from appearance energy data requires the use of either the thermal electron convention or the ion convention (also called stationary electron convention). The former assumes that the standard enthalpy of formation of the gaseous electron is zero at all temperatures and that an electron gas follows Boltzmann statistics (i.e. \( H^o_{298} - H^o_0 = 2.5RT = 6.20 \) kJ mol\(^{-1}\)). The use of the ion convention is equivalent to assuming that \( H^o_{298} - H^o_0 = 0 \). Therefore, for cations and anions, the relationships between enthalpies of formation at \( T = 298.15 \) K are, respectively:

\[
\Delta_f H^o(A^+, g)_{\text{IC}} = \Delta_f H^o(A^+, g)_{\text{TC}} - 6.20 \text{ kJ mol}^{-1}
\]

\[
\Delta_f H^o(A^-, g)_{\text{IC}} = \Delta_f H^o(A^-, g)_{\text{TC}} + 6.20 \text{ kJ mol}^{-1}
\]
If it is considered that the electron gas follows Fermi-Dirac statistics the constant 6.20 kJ mol\(^{-1}\) is replaced by 3.15 kJ mol\(^{-1}\).

(7) The standard enthalpy of formation of \(A^+\) at \(T = 298.15\) K can be accurately calculated from \(A_{E_0}(A^+, 0\) K\) in the absence of a kinetic shift and a reverse activation barrier, by using the equation:

\[
\Delta_r H^0(A^+, g) = A_{E_0}(A^+, 0\) K\) - \(\Delta_r H^0(B, g) + \Delta_r H^0(AB, g) + \int_0^{298} C^o_p(A^+)dT + \int_0^{298} C^o_p(B)dT - \int_0^{298} C^o_p(AB)dT.
\]

This equation uses the ion convention and assumes that the internal (rotational and vibrational) energy of \(AB\) are effective in causing dissociation. The last integral, which accounts for the translational heat capacity of \(AB\), is equal to \(2.5RT = 6.20\) kJ mol\(^{-1}\).

23. PULSED HIGH PRESSURE MASS SPECTROMETRY (PHPMS) [35,81-84]

**Measured quantities**
- Ion intensities at one or several temperatures.

**Primary quantities derived**
- Equilibrium constants. Rate constants.

**Secondary quantities derived**
- Gibbs energies and enthalpies of reaction. Bond dissociation enthalpies.

**Application**
- Species in the gas phase.

**Examples/Comments**
(1) Reaction equilibria involving ion-molecule reactions can be studied by PHPMS. In this technique the ion source contains a bath gas (e.g., methane) and the neutral reactants at a total pressure of \(ca.\) 500-1000 Pa. The electron pulses produce mainly positive ions and secondary electrons from the bath gas. These are thermalized by several collisions with the bath gas and some are captured by the neutral reactants, which are then thermalized and reach equilibrium. The measurement of equilibrium constants leads to Gibbs energies or to enthalpies of reaction (see examples under Equilibrium in the Gas Phase, Ion Cyclotron Resonance Mass Spectrometry, and Flowing Afterglow-Selected Ion-Flow Tube).

(2) The equilibrium constant for the reaction

\[
X(g) + Y^-(g) = X^-(g) + Y(g)
\]

can be determined at one or several temperatures. In either case it is possible to evaluate the enthalpy of reaction, from a van’t Hoff plot or by calculating the entropies of reactants and products. The enthalpy of reaction can be expressed in terms of the electron attachment enthalpy difference:

\[
\Delta_r H^0 = \Delta_{at} H^0(Y^-) - \Delta_{at} H^0(X^-)
\]
The electron attachment values are usually identified with adiabatic electron affinities (which are defined at $T = 0$ K). This implies negligible geometry changes between the neutral species and the anion.

(3) The same methodology (charge-transfer equilibria) can be used to determine ionization energies.

24. REACTION-SOLUTION CALORIMETRY (RSC) [13,33]

<table>
<thead>
<tr>
<th>Measured quantities</th>
<th>Temperature vs. time or heat flux.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary quantities derived</td>
<td>Enthalpies of reactions in solution.</td>
</tr>
<tr>
<td>Secondary quantities derived</td>
<td>Bond dissociation enthalpies. Mean bond dissociation enthalpies.</td>
</tr>
</tbody>
</table>

Application
Long-lived species in solution.

Examples/Comments
(1) See Titration Calorimetry, regarding isoperibol and isothermal calorimetry.
(2) The standard enthalpy of reaction equals the $M-X$ bond dissociation enthalpy in solution:

$$MX_n(sln) \rightarrow MX_{n-1}(sln) + X(sln)$$

$$\Delta_r H^o = D_{H_{sln}}^o (M-X)$$

(3) The standard enthalpy of reaction reflects a balance of several bond dissociation enthalpies in solution:

$$MX_n(sln) + AB(sln) \rightarrow MX_{n-1}A(sln) + XB(sln)$$

$$\Delta_r H^o = D_{H_{sln}}^o (M-X) + D_{H_{sln}}^o (A-B) - D_{H_{sln}}^o (M-A) - D_{H_{sln}}^o (X-B)$$

(4) The standard enthalpy of reaction reflects a balance of several bond dissociation enthalpies and mean bond dissociation enthalpies in solution:

$$MX_n(sln) + Y_2(sln) \rightarrow MX_{n-2}Y_2(sln) + X_2(sln)$$

$$\Delta_r H^o = 2D_{H_{sln}}^o (M-X) + D_{H_{sln}}^o (Y-Y) - 2D_{H_{sln}}^o (M-Y) - D_{H_{sln}}^o (X-X)$$

(5) The quantities in the previous examples can also be obtained in the gas phase if the relevant solvation enthalpies are available.

25. SINGLE-PULSE SHOCK TUBES (SPST) [64,85,86]

<table>
<thead>
<tr>
<th>Measured quantities</th>
<th>Concentration vs. time at several temperatures.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary quantities derived</td>
<td>Rate constants. Enthalpies of activation.</td>
</tr>
<tr>
<td>Secondary quantities derived</td>
<td>Enthalpies of reaction. Bond dissociation enthalpies.</td>
</tr>
<tr>
<td>Application</td>
<td>Neutral species in the gas phase.</td>
</tr>
</tbody>
</table>

Examples/Comments
(1) In SPST experiments the molecules MXₙ are thermally activated by a sudden compression caused by expansion of a gas at high pressure. As in the case of LPHP, the homogeneous heating and the short reaction times eliminate wall effects. The reaction temperature can be measured by using an internal standard, i.e. a reaction whose Arrhenius parameters are well known and which has rates similar to the decomposition of MXₙ. The ratio between the activation energies of the sample decomposition and the standard is obtained from the ratios of the respective rate constants vs. temperature. Concentrations may be monitored by gas chromatography.

\[ \text{MX}_n(g) \rightarrow \text{MX}_{n-1}(g) + X(g) \]

The pressure ranges used in SPST experiments are usually sufficiently high to avoid the fall-off correction of the Arrhenius activation energy (see Very Low Pressure Pyrolysis).

(2) The high pressure limit of the activation energy, \( E_a(T) \), for the above decomposition reaction is usually measured at temperatures well above 298.15 K, in the temperature range of ca. 500-1500 K (\( T \) is the mean of the experimental temperature interval). The enthalpy of reaction at \( T = 298.15 \) K can be derived from the equation:

\[ D_H^o(M - X) = E_a(T) - (T - 298.15)(\Delta C_p^o) - T(\Delta C_p^{eo}) \]

by assuming that the activation internal energy for the reverse reaction at \( T = 0 \) K is zero. The second term includes the average molar heat capacity difference between products and reactants in the \( T - 298.15 \) K temperature range, and the last term includes the average molar heat capacity difference between the transition state and the products in the \( 0 - T \) K temperature range. These heat capacities can be calculated by statistical mechanics or derived from empirical methods.

(3) A different method of calculating the bond dissociation enthalpy at temperature \( T \) from the measured \( E_a(T) \) consists simply in using the equation

\[ \Delta H_T^o = E_{a-1}(T) - E_{a-1}(T) + RT \]

where \( E_{a-1}(T) \) is the activation energy for the reverse (radical recombination) reaction. In the absence of a reliable value for \( E_{a-1}(T) \), it is probably a better approach to rely on the assumption described in (2).

26. TITRATION CALORIMETRY [87-89]

**Measured quantities**
- Temperature (or heat flux) vs. quantity of titrant added.

**Primary quantities derived**
- Reaction enthalpies and equilibrium constants.

**Secondary quantities derived**
- Bond dissociation enthalpies. Mean bond dissociation enthalpies.

**Application**
- Long-lived species in solution.

**Examples/Comments**

(1) There are two types of titration calorimetry: isoperibol and isothermal. Isoperibol calorimetry is based on the continuous monitoring of the temperature of the contents of an adiabatic reaction vessel. Isothermal calorimetry is based on the continuous monitoring of heat flux between the reaction vessel and its surroundings, keeping the reaction vessel and its contents
at a constant temperature (equal to the temperature of the surroundings). Isothermal calorimetry has the advantage over isoperibol calorimetry that no heat capacity measurements are required and no corrections are necessary for the heat exchange between the reaction vessel and its environment.

(2) There are two types of titrant addition: incremental and continuous. In the first type the titrant is added incrementally and the temperature is usually readjusted to the initial temperature before each additional increase is added. This procedure has the advantage that reactions which are kinetically hindered may be accurately studied. In continuous titration, the titrant is introduced at constant rate during a run. This continuous addition of the titrant has the advantage that a complete record of the heat effects during a reaction is obtained.

(3) The addition of the titrant to the titrate solution produces one or more reactions. The extent of the reaction(s) and the energy produced are related to the corresponding equilibrium constant(s) and enthalpy change(s). The equations relating the heat produced, the equilibrium constant(s) and the enthalpy change(s) for the reaction(s) are generally complex. It is convenient to express the relationship among these quantities, for the general case of n reactions occurring in the reaction vessel, as

\[ Q_{c,p} = \sum_{i=1}^{n} \Delta H_i \Delta n_{i,p} \]

where \( \Delta n_{i,p} \) is the change in the moles of the product \( i \) formed since the beginning of the reaction to the considered point \( p \) and is a function of the equilibrium constant for reaction \( i \). In general, the best values for \( \Delta H \) are calculated by a least squares analysis of the equation.

(4) It has been shown that selective titrants can be used for studying metal-ligand interactions of almost any magnitude.

27. VERY LOW PRESSURE PYROLYSIS (VLPP) [64,90,91]

Measured quantities
Concentration vs. time at several temperatures.

Primary quantities derived
Rate constants. Enthalpies of activation.

Secondary quantities derived
Enthalpies of reaction. Bond dissociation enthalpies.

Application
Neutral species in the gas phase.

Examples/Comments
(1) In VLPP experiments the molecule MX\(_n\) is thermally activated by collisions with the heated walls of a reactor cell. This activation leads to decomposition:

\[ MX_n(g) \rightarrow MX_{n-1}(g) + X(g) \]

the products being analysed by mass spectrometry. The process occurs at low pressure (ca. 0.1 Pa), to ensure that MX\(_n\) may collide many times with the walls without hitting another molecule or decomposition fragment. However, as a result of this low pressure, the number of collisions is not enough to obtain an equilibrium energy distribution, implying that the rate constant increases when the pressure is raised. This fall-off effect is handled by using RRKM theory, which provide
a relationship between the rate constant at the experimental pressure and the high pressure limit rate constant. By assuming a value for the Arrhenius factor, the activation energy (at infinite pressure) is adjusted, so that good agreement between the theoretical and experimental values of the rate constant vs. temperature is obtained.

(2) The high-pressure limit of the activation energy, $E_a(T)$, for the above decomposition reaction is usually determined at temperatures well above 298.15 K ($T$ is the mean of the experimental temperature interval). The enthalpy of reaction at $T = 298.15$ K is derived as described for the Single-Pulse Shock Tubes.

(3) VLPP results may be affected by surface reactions at the walls of the reactor.

Acknowledgments

The large amount of work done by Professor J. Martinho Simões, University of Lisbon, Portugal, for the definition of the structure of this manuscript is deeply acknowledged.
INDEX OF SYMBOLS

The index presents the suggested symbols for some physical quantities together, in the last column, with the symbols which, for the same physical quantity, are often used in the literature, but which should not encouraged to be used, because of the possible confusion with the products of two symbols. As the quantities considered are usually molar quantities the subscript "m" is omitted in most of them. Also, the indication of the temperature of a certain physical quantity is dropped when the temperature is 298.15 K.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name of physical quantity</th>
<th>Symbol not encouraged</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{e_0}(A^+, 0 \text{ K})$</td>
<td>Appearance energy of $A^+$ at $T = 0 \text{ K}$</td>
<td>$AE_{e_0}(A^+)$</td>
</tr>
<tr>
<td>$D_{G_{sln}}(R-H)$</td>
<td>R–H dissociation Gibbs energy in solution</td>
<td>$DG_{sln}(R-H)$</td>
</tr>
<tr>
<td>$D^o_{H,(T)}$</td>
<td>Molar bond dissociation enthalpy at temperature $T \text{ K}$</td>
<td>$DH^o_i$</td>
</tr>
<tr>
<td>$D^o_{Hij}$</td>
<td>A–B molar bond dissociation enthalpy at temperature $T \text{ K}$</td>
<td>$DH^o_i(A-B)$</td>
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<tr>
<td>$D^o_{H_{sln}}$</td>
<td>Stepwise bond dissociation enthalpy</td>
<td>$DH^o_i$</td>
</tr>
<tr>
<td>$D^o_{H_{sln}}$</td>
<td>Bond dissociation enthalpy in solution</td>
<td>$DH^o_i$</td>
</tr>
<tr>
<td>$D_H^o$ or $\langle D_H^o \rangle$</td>
<td>Mean bond dissociation enthalpy</td>
<td>$\overline{DH^o}$ or $\langle DH^o \rangle$</td>
</tr>
<tr>
<td>$D^o_{U,(T)}$</td>
<td>Mean bond dissociation internal energy at temperature $T \text{ K}$</td>
<td>$DU^o_i$</td>
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<tr>
<td>$D^o_{U_{ij}}(A-B, T)$</td>
<td>A–B molar bond dissociation internal energy at temperature $T \text{ K}$</td>
<td>$DU^o_i(A-B)$</td>
</tr>
<tr>
<td>$E(M-L)$</td>
<td>M–L bond enthalpy contribution or M–L bond enthalpy term</td>
<td></td>
</tr>
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<td>$E_{ea}$</td>
<td>Adiabatic electron affinity</td>
<td></td>
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<tr>
<td>$E_i$</td>
<td>Adiabatic ionization energy</td>
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<td>$E_S(R-H)$</td>
<td>Intrinsic bond strength or bond snap enthalpy</td>
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<td>Gas phase acidity of AH</td>
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<tr>
<td>$\Delta_{base}G^o(A)$</td>
<td>Gas phase basicity of A</td>
<td>$GB(A)$</td>
</tr>
<tr>
<td>$\Delta_{att}H$</td>
<td>Electron attachment enthalpy</td>
<td></td>
</tr>
</tbody>
</table>
References

49. B. S. Freiser In *Bonding Energetics in Organometallic Compounds*; T. J. Marks, Ed.; ACS Symposium Series No. 428; Washington, D.C., 1990; Chapter 4.