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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY
PHYSICAL AND BIOPHYSICAL CHEMISTRY DIVISION

THERMOCHEMISTRY of CHEMICAL REACTIONS:

II. EXPERIMENTAL METHODS FOR THE DETERMINATION of BOND ENERGIES[1]

(IUPAC Technical Report)

Prepared for publication by:
MANUEL A. V. RIBEIRO DA SILVA[‡]

Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal.

[‡]Corresponding author: E-mail: risilva@fc.up.pt

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Thermochemistry of Chemical Reactions:

II. Experimental Methods for the Determination of Bond Energies[1]

(IUPAC Technical Report)

Abstract: This work, which is presented in two parts, is concerned with the most currently used experimental techniques for the study of the thermochemistry of chemical reactions. The first part, IUPAC Recommendations, deals with terminology and symbols, and discusses the meaning, designation and symbols of the different parameters used in molecular thermodynamic studies. This second part is a brief description of the most important methods used to investigate the thermodynamic stability of molecules and chemical bonds, together with a detailed analysis of its basic assumptions and how thermodynamic quantities are derived.

INTRODUCTION.

When Thermochemistry started in the 18th century it was limited to the study of the chemical reactions, and so calorimetry was the experimental technique for such studies. For many years the aim of thermochemistry was to provide accurate thermal data on chemical compounds of practical importance, mainly by calorimetric and equilibrium studies. Lately, during the last three or four decades of the 20th century, the scope was considerably extended as the result of the developments of microcalorimetric techniques, of flow calorimetry, of titration calorimetry and of high temperature calorimetry, with considerable impact in biochemical studies, in metallurgical studies, in organometallic and inorganic thermochemistry and in other applied fields. A parallel development has led to the increase output of significant thermal data on gas-phase transient species, like free radicals, radical ions, etc, by kineticists and by use of photoionization spectroscopy, mass spectroscopy and ion-cyclotron resonance. Although outside the scope of the traditional calorimetric methods, the data that became available from those techniques, together with the traditional thermochemical data, enable bond energies to be evaluated and the inter-relation of molecular structure and bonding energy to be examined, thus leading to the development of Molecular Energetics, which is concerned with the study of the thermodynamic stability of molecules and chemical bonds.

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.

The first part of this report deals with the meaning, designation, and symbols of the different parameters used in molecular thermochemistry studies. This second part includes brief descriptions 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. Substantial parts of the text were quoted from references [1,2]

1. EXPERIMENTAL METHODS FOR THE DETERMINATION OF BOND ENERGIES. A SCHEMATIC OVERVIEW

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

Table 1   Experimental methods addressed.

Condensed phase methods	Gas phase methods
Combustion Calorimetry (CC)	Birge-Sponer Extrapolation (BS)
Differential Scanning Calorimetry (DSC)	Electron Impact Mass Spectrometry (EIMS)
Electrochemical Measurements (EChem)	Electron Photodetachment Spectroscopy (EPDS)
Equilibrium in Solution (ES)	Equilibrium in the Gas Phase (EG)
Kinetics in Solution (KS)	Flowing Afterglow - Selected Ion-Flow Tube (FA-SIFT)
Photoacoustic Calorimetry (PAC)	Guided Ion Beam Mass Spectrometry (GIBMS)
Photocalorimetry (PC)	High Pressure Mass Spectrometry (HPMS)
Reaction-Solution Calorimetry (RSC)	Ion Cyclotron Resonance Mass Spectrometry (ICR)
Titration Calorimetry (TC)	Kinetic Energy Release Distributions (KERD)
	Kinetics in the Gas Phase (KG)
	Knudsen Cell – Mass Spectrometry (KC-MS)
	Laser-Powered Homogeneous Pyrolysis (LPHP)
	Mass Spectrometry - Kinetic Method (MS-K)
	Photoelectron Spectroscopy (PES)
	Photoionization Mass Spectrometry (PIMS)
	Pulsed High Pressure Mass Spectrometry (PHPMS)
	Single-Pulse Shock Tubes (SPST)
	Very Low Pressure Pyrolysis (VLPP)

2.   BIRGE-SPONER EXTRAPOLATION (BS) [3,4]

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 one-dimensional anharmonic oscillator model:

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$$\varepsilon = \left(v + \frac{1}{2}\right) h v - \left(v + \frac{1}{2}\right)^2 x_e h v + \dots$$

where x_e is the anharmonicity constant and v is the frequency. When $\Delta\varepsilon = \varepsilon(v+1) - \varepsilon(v) = \varepsilon(v) - \varepsilon(v-1)$ it can be shown that the maximum value of v is given by

$$v_{max} = \frac{1 - x_e}{2 x_e}$$

and therefore

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

$$E_{d,0} = E(v_{max}) - E(0) = \frac{h v_e}{4 x_e} - \frac{h v_e}{2}$$

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:

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

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

(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 ε vs. v are ignored. As a result, the dissociation quantum number, as calculated above, is often higher than the true value. The described calculation is an estimation of the upper limit to E_d. Birge and Sponer suggested an extrapolation of all the available $E(v+1)$ values against v which leads to more realistic estimates of E_d.

3.   COMBUSTION CALORIMETRY (CC) [5,6-10]

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 MX_{n-1} and X are available, the first M−X molar bond dissociation enthalpy can be calculated:

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

$$\Delta_r H_m^o = \Delta_f H_m^o(MX_{n-1}, g) + \Delta_f H_m^o(X, g) - \Delta_f H_m^o(MX_n, g) = D_{H,m}^o(M-X)$$

(3)   Same situation of the previous example, but only the standard molar enthalpies of formation of the gaseous species M and X are available. The mean M−X molar bond dissociation enthalpy, $\langle D_{H,m}^o \rangle(M-X)$, can be derived:

$$MX_n(g) \rightarrow M(g) + nX(g)$$

$$\Delta_r H_m^o = \Delta_f H_m^o(MX, g) + n\Delta_f H_m^o(X, g) - \Delta_f H_m^o(MX_n, g) = n\langle D_{H,m}^o \rangle(M-X)$$

4.   DIFFERENTIAL SCANNING CALORIMETRY (DSC) [11]

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:

$$ML_nX_m(cr) = MX_m(cr) + nL(g)$$

If the enthalpy of this decomposition reaction ($\Delta_{dec}H^o$) 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 M−L bond dissociation enthalpy:

$$n\langle D_{H,m}^o \rangle(M-L) = \Delta_{dec}H_m^o + \Delta_{sub}H_m^o(MX_m) - \Delta_{sub}H_m^o(ML_nX_m)$$

(3)   It is important to notice that the measured $\Delta_{\text{dec}}H^{\circ}$ values usually refer to temperatures well above $T = 298.15$ K. The temperature correction requires heat capacity data for ML_nX_m, MX_m, and L.
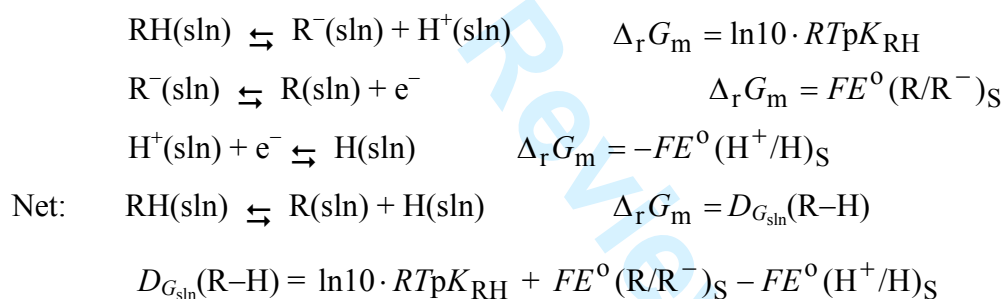
(4)   DSC has also been used to study other types of reaction such as ligand replacements and isomerizations.

5.   ELECTROCHEMICAL MEASUREMENTS (ECHEM) [12-17]

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 (All cell potentials are given relative to the standard hydrogen electrode):

$$RH(\text{sln}) \rightleftharpoons R^-(\text{sln}) + H^+(\text{sln}) \qquad \Delta_r G_m = \ln 10 \cdot RT pK_{RH}$$

$$R^-(\text{sln}) \rightleftharpoons R(\text{sln}) + e^- \qquad \Delta_r G_m = FE^{\circ}(R/R^-)_S$$

$$H^+(\text{sln}) + e^- \rightleftharpoons H(\text{sln}) \qquad \Delta_r G_m = -FE^{\circ}(H^+/H)_S$$

Net: $$RH(\text{sln}) \rightleftharpoons R(\text{sln}) + H(\text{sln}) \qquad \Delta_r G_m = D_{G_{\text{sln}}}(R-H)$$

$$D_{G_{\text{sln}}}(R-H) = \ln 10 \cdot RT pK_{RH} + FE^{\circ}(R/R^-)_S - FE^{\circ}(H^+/H)_S$$

The application of this equation requires an estimate of the reduction potential of H^+ in the same solvent where the experiments were carried out. $E^{\circ}(H^+/H)_S$ 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):

$$-FE^{\circ}(H^+/H)_S = \Delta_f G_m^{\circ}(H,g) + \Delta_{\text{sln}}G_m(H,g) + \Delta_{\text{transf}}G_m(H^+, S \rightarrow \text{aq})$$

Once $D_{G_{\text{sln}}}(R-H)$ 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.

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

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

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

$$D_{H,m}^{o}(R-H) = \ln 10 \cdot RTpK_{RH} + FE_{E}^{o}(R/R^{-})_{S} + \Delta_{transf}G_{m}(H^{+}, S \to aq) + \Delta_{f}H_{m}^{o}(H,g)$$
$$+ 0.5TS_{m}^{o}(H_{2},g) + T\left[S_{m}^{o}(R,g) - S_{m}^{o}(RH,g)\right] + T\left[\Delta_{sln}S_{m}(R,g) - \Delta_{sln}S_{m}(RH,g)\right]$$
$$+ \Delta_{sln}H_{m}(RH,g) - \Delta_{sln}H_{m}(R,g)$$

(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 kJ·mol^{-1}) illustrates this procedure for S = dimethyl sulfoxide and when the oxidation potential of R^{-} is referred to the ferrocene/ferrocenium (Fc/Fc^{+}) couple instead of the SHE in water.

$$D_{H,m}^{o}(R-H) = 2.303RTpK_{RH} + FE_{Fc/Fc^{+}}^{o}(R/R^{-})_{DMSO} + 306.7 \text{ kJ·mol}^{-1}$$

(4)   The pK_{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, $D_{G_{sln}}^{o}(X-H) - D_{G_{sln}}^{o}(Y-H)$ or $D_{H}^{o}(X-H) - D_{H}^{o}(Y-H)$. These data should rely on redox potentials and pK_{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 $D_{G_{sln}}^{o}(X-H^{+})$ and $D_{G_{sln}}^{o}(X^{-}-H)$, identified with the Gibbs energies of the reactions

$$RH^{+}(sln) \rightleftharpoons R(sln) + H^{+}(sln)$$
$$RH^{-}(sln) \rightleftharpoons R^{-}(sln) + H(sln)$$
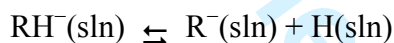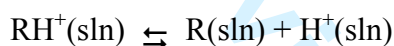
can also be obtained by measuring the redox potentials of RH.

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

$$X(sln) + Y^{-}(sln) \rightleftharpoons X^{-}(sln) + Y(sln)$$
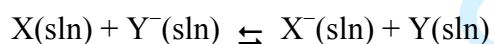
6.   ELECTRON IMPACT MASS SPECTROMETRY (EIMS) [18,19]

Measured quantities   Ion intensities vs. electron energy.
Primary quantities derived   Appearance energies.
Secondary quantities derived   Enthalpies of reaction. Bond dissociation enthalpies.
Application   Species in the gas phase.
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^+, $A_E(A^+)$, measured by electron impact,

$$AB(g) + e^- \rightarrow A^+(g) + B(g) + 2e^-$$
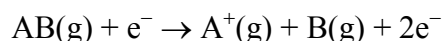
can be related to the A–B bond dissociation enthalpy at $T = 298.15$ K without any further correction. $E_i(A)$ is the adiabatic ionization energy of A.

$$D_H^o(A-B) = A_E(A^+) - E_i(A)$$

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

$$\Delta_f H^o(A^+,g) = A_E(A^+) - \Delta_f H^o(B,g) + \Delta_f H^o(AB,g)$$

7.   ELECTRON PHOTODETACHMENT SPECTROSCOPY (EPDS) [20-22]

Measured quantities   Ion currents throughout 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

$$A^-(g) \xrightarrow{h\nu} A(g) + e^-$$
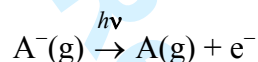
is monitored as a function of the photon energy. The anions may be trapped in the cell of an ion cyclotron resonance mass spectrometer and their signal intensity is measured with and without irradiation and converted to the photodetachment cross section. This cross section vs. the radiation wavelength 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.

8.   EQUILIBRIUM IN THE GAS PHASE (EG) [23-25]

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:

$$MX_n(g) + AB(g) \leftrightarrows MX_{n-1}A(g) + XB(g)$$
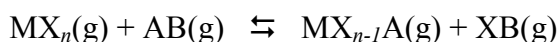
$$\Delta_r H_T^o = D_H^o(M-X, T) + D_H^o(A-B, T) - D_H^o(M-A, T) - D_H^o(X-B, T)$$

(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

$$XH^+(g) + Y(g)) \leftrightarrows YH^+(g) + X(g)$$
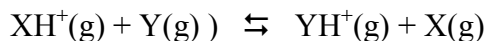
equals the difference between the proton affinities of X and Y, which is equivalent to a bond dissociation enthalpy difference:

$$\Delta_r H_m^o = E_{pa}(X) - E_{pa}(Y) = D_H^o(X-H^+) - D_H^o(Y-H^+)$$

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).

## 9.   EQUILIBRIUM IN SOLUTION (ES) [5,23,26]

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.

10.   FLOWING AFTERGLOW - SELECTED ION-FLOW TUBE (FA-SIFT) [27-31]

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

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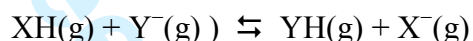
can be determined at one or several temperatures, usually by measuring the forward and the reverse rate constants. In either case it is possible to evaluate the enthalpy of reaction, from a van't Hoff plot or by calculating the entropies of reactants and products. The enthalpy of reaction can be expressed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

$$\Delta_r H_m^o = D_H^o(X^- - H^+) - D_H^o(Y^- - H^+)$$

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

$$D_H^o(X - H) = D_H^o(X^- - H^+) + E_{ea}(X) - E_i(H)$$

(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 $D_H^o(Y^- - H^+) \geq D_H^o(X^- - H^+) \geq D_H^o(Z^- - H^+)$.

11.   GUIDED ION BEAM MASS SPECTROMETRY (GIBMS) [32,33]

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)

$$M^+(g) + AB(g) \rightarrow MB^+(g) + A(g)$$
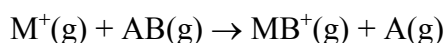
can be obtained from the threshold energy (E_0), by assuming that there are no activation barriers in excess of the positive enthalpy of the reaction:

$$D_H^o(\text{M}^+ - \text{B, 0 K}) = D_H^o(\text{A} - \text{B, 0 K}) - E_0$$

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, σ_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 σ_0, n, and E_0 are optimized by using a non-linear least squares analysis.

(2)   The threshold of the reaction

$$\text{M}^+(\text{g}) + \text{AB}(\text{g}) \rightarrow \text{MB}(\text{g}) + \text{A}^+(\text{g})$$
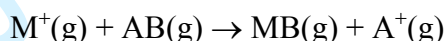
affords the bond dissociation enthalpy in the neutral species MB.

(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):

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

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.

12. HIGH PRESSURE MASS SPECTROMETRY (HPMS) [34-37]

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

$$\text{MX}_{n-1}^+(\text{g}) + \text{X}(\text{g})) \leftrightarrows \text{MX}_n^+(\text{g})$$
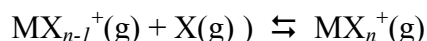
obtained from a van't Hoff plot, is equal to $-D_H^o(X_{n-1}M^+ - X)$.

13. ION CYCLOTRON RESONANCE MASS SPECTROMETRY (ICR) [38-42]

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

$$XH^-(g) + Y(g)) \leftrightarrows YH^-(g) + X(g)$$
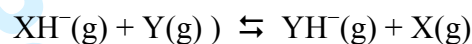
equals the difference between the hydride affinity (H_A) of X and Y, which is equivalent to a bond dissociation enthalpy difference:

$$\Delta_r H^o = H_A(X) - H_A(Y) = D_H^o(X - H^-) - D_H^o(Y - H^-)$$

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, $E_{ea}(X)$, is available:

$$D_H^o(X^- - H) = D_H^o(X - H^-) - E_{ea}(X) + E_{ea}(H)$$

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

$$D_H^o(X - H) = D_H^o(X - H^-) - E_{ea}(XH) + E_{ea}(H)$$

(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):

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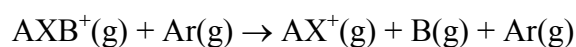
The threshold for the formation of AX$^+$ can be identified with the AX$^+$–B bond dissociation enthalpy if both AXB$^+$ and AX$^+$ are in their ground states. Competitive CID experiments, providing limits to bond dissociation enthalpies, can also be made:

$$AXB^+(g) + Ar(g) \rightarrow AX^+(g) + B(g) + Ar(g)$$

$$AXB^+(g) + Ar(g) \rightarrow BX^+(g) + A(g) + Ar(g)$$
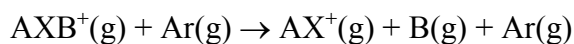
If the signal intensity for AX^+ is larger than for BX^+, then $D_H^o(BX^+ - A) > D_H^o(AX^+ - B)$.

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

(6) 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.

(7) It is usually assumed than ICR results refer to $T = 298.15$ K.

14. KINETIC ENERGY RELEASE DISTRIBUTIONS (KERD) [43]

Measured quantities   Ion intensities vs. product kinetic energy.
Primary quantities derived
Secondary quantities derived Enthalpies of reaction. Bond dissociation enthalpies.
Application   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 $(MX_n^+)^*$ was formed with internal excess energy by an exothermic reaction. Its decomposition in the field-free region,

$$(MX_n^+)^*(g) \rightarrow MX_{n-1}^+(g) + X(g)$$

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.

15. KINETICS IN THE GAS PHASE (KG) [44-47]

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

14

(1)   The enthalpy of activation of a reaction can be derived from an Eyring plot, i.e. a plot of $\ln(k/T^n)$ vs. $1/T$ (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.

16.   KINETICS IN SOLUTION (KS) [23,26,48]

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.

17.   KNUDSEN CELL - MASS SPECTROMETRY (KC-MS) [49-51]

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:

$$\Delta_r G_T^o = \Delta_r H_T^o - T\Delta_r S_T^o = -RT \ln K_p(T)$$

This equation transforms into

$$\Delta_r H_T^o = -RT \ln K_p(T) - T\sum_i v_i \left\{ \left[G_i^o(T) - H_i^o(298) \right] / T \right\}$$

Where v_i is the stoichiometric coefficient of species i, and $\left[G_i^o(T) - H_i^o(298) \right] / T$ is the Gibbs energy function of species i. 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 $\Delta_r H^o$ (at $T = 298.15$ K), one for each temperature of measurement. The average value of $\Delta_r H^o$ is then used to derive the standard molar enthalpy of formation of the species of interest (from which bond enthalpy data can be obtained).

18.   LASER-POWERED HOMOGENEOUS PYROLYSIS (LPHP) [52-54]

Measured quantities	Concentration vs. time at several temperatures.
Primary quantities derived	Enthalpies of activation.
Secondary quantities derived	Enthalpies of reaction. Bond dissociation enthalpies.
Application	Neutral species in the gas phase.

Examples/Comments

(1)   In LPHP experiments the molecule MX_n 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 CO_2-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:

16

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

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 MX_n. 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, $E_a(T)$, 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:

$$D_H^o(M-X) = E_a(T) - (T - 298)\langle \Delta_r C_p^o \rangle - T \langle \Delta^{\neq} C_{V,-1}^o \rangle$$

by assuming that the internal energy of activation ($\Delta^{\neq} U_{-1}^o$) 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 K T 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.

19.   MASS SPECTROMETRY - KINETIC METHOD (MS-K) [55]

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

$$\ln \left[\frac{XH^+}{BH^+} \right] \approx \left[E_{pa}(X) - E_{pa}(B) \right] C$$

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.

20.   PHOTOACOUSTIC CALORIMETRY (PAC) [56-59]

Measured quantities   Amplitude of photoacoustic signal and solution
                                   transmitance.
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

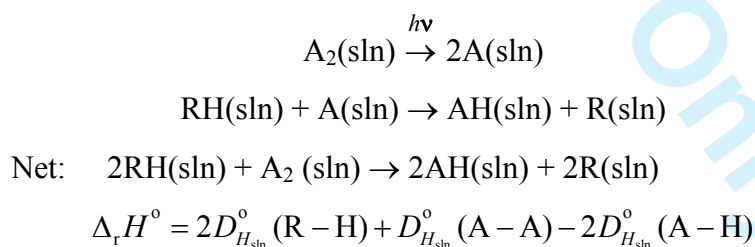$$E_o = N_A h\nu = \Phi_{nr} E_o + \Phi_f E_f + \Phi_u E_u$$

where $N_A h\nu$ is the molar pulse energy, Φ_{nr} is the "non-radiative quantum yield", evaluated from the experimental data, and the product $\Phi_{nr} E_o$ represents the observed energy 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 ($\Delta_r H^o$ for a chemical reaction).

(2)   In order to derive the true value of Φ_{nr}, 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:

$$XY(sln) \xrightarrow{h\nu} X(sln) + Y(sln)$$

$$\Delta_r H^o = D^o_{H_{sln}}(X-Y)$$
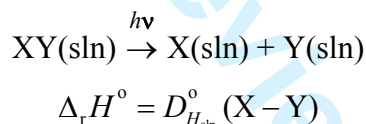
(4)   The enthalpy of the net reaction is measured and identified with a balance of several bond dissociation enthalpies in solution (for example, A$_2$ is di-*tert*-butyl peroxide and RH is phenol):

$$A_2(sln) \xrightarrow{h\nu} 2A(sln)$$

$$RH(sln) + A(sln) \rightarrow AH(sln) + R(sln)$$

Net: $2RH(sln) + A_2(sln) \rightarrow 2AH(sln) + 2R(sln)$

$$\Delta_r H^o = 2D^o_{H_{sln}}(R-H) + D^o_{H_{sln}}(A-A) - 2D^o_{H_{sln}}(A-H)$$

(5)   It is often assumed that the solvation enthalpies cancel, so that the bond dissociation enthalpies are close to the gas phase values.

21.   PHOTOCALORIMETRY (PC) [60-63]

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.

22. PHOTOELECTRON SPECTROSCOPY (PES) [64-67]

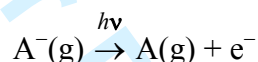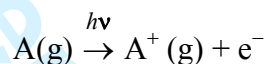*Measured quantities*   Electron count vs. electron kinetic energy.

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

$$A(g) \xrightarrow{h\nu} A^+(g) + e^-$$

$$A^-(g) \xrightarrow{h\nu} A(g) + e^-$$

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 $0 \leftarrow 0$ 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.

23. PHOTOIONIZATION MASS SPECTROMETRY (PIMS) [68-71]

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 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.

$$AB(g) \xrightarrow{h\nu} A^+(g) + B(g) + e^-$$
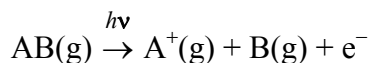
$$D_H^o(\text{A} - \text{B, 0 K}) = A_{E_0}(\text{A}^+, \text{0 K}) - E_i(\text{A}) + \langle E_i \rangle$$

$\langle E_i \rangle$ 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:

$$D_H^o(\text{A}^+ - \text{B, 0 K}) = A_{E_0}(\text{A}^+, \text{0 K}) - E_i(\text{AB}) + \langle E_i \rangle$$

(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 $A_{E0}(\text{A}^+)$ 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} 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. $H_{298}^o - H_0^o = 2.5RT = 6.20$ kJ·mol^{-1}). The use of the ion convention is equivalent to assuming that $H_{298}^o - H_0^o = 0$. Therefore, for cations and anions, the relationships between enthalpies of formation at $T = 298.15$ K are, respectively:

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

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

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 $A_{E0}(\text{A}^+, \text{0 K})$ in the absence of a kinetic shift and a reverse activation barrier, by using the equation:

$$\Delta_f H^o(\text{A}^+, \text{g}) = A_{E_0}(\text{A}^+, \text{0 K}) - \Delta_f H^o(\text{B,g}) + \Delta_f H^o(\text{AB,g})$$

$$+ \int_0^{298} C_p^o(\text{A}^+)dT + \int_0^{298} C_p^o(\text{B})dT - \int_0^{298} C_{p,\text{trans}}^o(\text{AB})dT$$

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}.

24.   PULSED HIGH PRESSURE MASS SPECTROMETRY (PHPMS) [25,72-75]

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

$$X(g) + Y^-(g) \; \leftrightharpoons \; X^-(g) + Y(g)$$
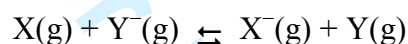
can be determined at one or several temperatures. In either case it is possible to evaluate the enthalpy of reaction, from a van't Hoff plot or by calculating the entropies of reactants and products. The enthalpy of reaction can be expressed in terms of the electron attachment enthalpy difference:

$$\Delta_r H^\circ = \Delta_{att} H^\circ(Y^-) - \Delta_{att} H^\circ(X^-)$$

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.

25.   REACTION-SOLUTION CALORIMETRY (RSC) [5,23]

|	
Measured quantities	Temperature vs. time or heat flux.
Primary quantities derived	Enthalpies of reactions in solution.
Secondary quantities derived	Bond dissociation enthalpies. Mean bond dissociation enthalpies.
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:

$$MX_n(\text{sln}) \rightarrow MX_{n-1}(\text{sln}) + X(\text{sln})$$
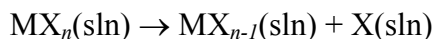
$$\Delta_r H^\circ = D_{H_{\text{sln}}}^\circ(M-X)$$

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

$$MX_n(\text{sln}) + AB(\text{sln}) \rightarrow MX_{n-1}A(\text{sln}) + XB(\text{sln})$$
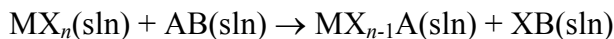
$$\Delta_r H^\circ = D_{H_{\text{sln}}}^\circ(M-X) + D_{H_{\text{sln}}}^\circ(A-B) - D_{H_{\text{sln}}}^\circ(M-A) - D_{H_{\text{sln}}}^\circ(X-B)$$

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

$$MX_n(\text{sln}) + Y_2(\text{sln}) \rightarrow MX_{n-2}Y_2(\text{sln}) + X_2(\text{sln})$$
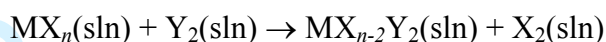
$$\Delta_r H^\circ = 2\langle D_{H_{\text{sln}}}^\circ\rangle(M-X) + D_{H_{\text{sln}}}^\circ(Y-Y) - 2\langle D_{H_{\text{sln}}}^\circ\rangle(M-Y) - D_{H_{\text{sln}}}^\circ(X-X)$$

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

26.   SINGLE-PULSE SHOCK TUBES (SPST) [54,76,77]

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 SPST experiments the molecules MX_n 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 MX_n. 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.

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

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:

$$D_H^\circ(M-X) = E_a(T) - (T-298.15)\langle\Delta C_p^\circ\rangle - T\langle\Delta C_{V,-1}^{\neq}\rangle$$

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 $\tilde{0}T$ 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

$$\Delta_r H_T^o = E_{a,1}(T) - E_{a,-1}(T) + RT$$

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).

27.   TITRATION CALORIMETRY [78-80]

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 ΔH 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.

28.   VERY LOW PRESSURE PYROLYSIS (VLPP) [54,81,82]

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

INDEX OF SYMBOLS

The index presents the recommended 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.

All physical quantities indicated below have dimensions of either molar energy or molecular energy. Where specific terms would be intended as molar quantities, they must be identified as such by the subscript 'm'.

Also, the indication of the temperature of a certain physical quantity is dropped when the temperature is 298.15 K.

Symbol	Name of physical quantity	Symbol not encouraged
$A_{E_0}(\text{A}^+, 0\text{ K})$	Appearance energy of A^+ at $T = 0$ K	$AE_0(\text{A}^+)$
$D_{G_{\text{sln}}}(\text{R–H})$	R–H dissociation Gibbs energy in solution	$DG_{\text{sln}}(\text{R–H})$
$D_{H,\text{m}}^{\text{o}}(T)$	Molar bond dissociation enthalpy at temperature T K	DH_T^{o}
$D_{U,\text{m}}^{\text{o}}(T)$	Molar bond dissociation energy, at temperature T K	DU_T^{o}
$D_U^{\text{o}}(\text{A–B}, T)$	A–B bond dissociation energy, at temperature T K	$DU_T^{\text{o}}(\text{A–B})$
$D_H^{\text{o}}(\text{A–B}, T)$	A–B bond dissociation enthalpy at temperature T K	$DH_T^{\text{o}}(\text{A–B})$
$D_{H_i}^{\text{o}}$	Stepwise bond dissociation enthalpy	DH_i^{o}
$D_{H,\text{sln}}^{\text{o}}$	Bond dissociation enthalpy in solution	$DH_{\text{sln}}^{\text{o}}$
$\overline{D_H^{\text{o}}}$ *or* $\langle D_H^{\text{o}}\rangle$	Mean bond dissociation enthalpy	$\overline{DH^{\text{o}}}$ *or* $\langle DH^{\text{o}}\rangle$
$E(\text{M–L})$	M–L bond enthalpy contribution *or* M–L bond enthalpy term	
$E_{\text{ea}}(\text{AB})$	Electron affinity (AB)	
$E_{\text{i}}(\text{AB})$	Ionization energy	
E_{pa}	Proton affinity	PA
E_{R}	Reorganization energy	ER
$E_{\text{S}}(\text{R–H})$	Intrinsic bond strength *or* bond snap enthalpy	
E_0	Threshold energy	
H_A	Hydride affinity	HA
$\Delta_{\text{acd}}G^{\text{o}}(\text{AH})$	Gas phase acidity of AH	
$\Delta_{\text{pba}}G^{\text{o}}(\text{A})$	Gas phase basicity of A	$GB(\text{A})$
$\Delta_{\text{att}}H^{\text{o}}$	Electron attachment enthalpy	

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