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Thermochemistry of Chemical Reactions: I. Terminology and Symbols

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

THERMOCHEMISTRY of CHEMICAL REACTIONS:
I. TERMINOLOGY AND SYMBOLS

(IUPAC Recommendations 200x)

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(IUPAC Recommendations 200x)

Abstract: This work, which is presented in two parts, is concerned with the most current experimental techniques for the study of the thermochemistry of chemical reactions. This first part of these Recommendations deals with terminology and symbols, and discusses the meaning and designation of, and symbols for the different parameters used in molecular thermodynamic studies. The second part is a Technical Report containing brief descriptions of the most important methods used to investigate the thermodynamic stability of molecules and chemical bonds.

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 investigation of 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 co-workers 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

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4 techniques to probe the energetics of these transient species have been developed in the
5 last three decades.

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

11 Terminology and symbols for “bond energies” are, at the moment, somewhat
12 confusing. However, these quantities are now widely used to estimate the
13 thermochemistry of chemical reactions involving species for which the standard enthalpies
14 of formation are unknown. The proliferation of designations and symbols, such as bond
15 strengths, bond enthalpies, bond energies, bond dissociation enthalpies, bond enthalpy
16 terms, stepwise bond dissociation energies, intrinsic bond energies, clearly requires some
17 standardization.

18 The first part of this series, IUPAC Recommendations, discusses the meaning and
19 designation of, and symbols for the different parameters used in molecular
20 thermochemistry studies. The second part, a Technical Report, includes a brief description
21 of the main experimental methods that have been used to derive data, together with a
22 detailed analysis of their basic assumptions and how thermodynamic quantities are
23 obtained. Substantial parts of the text were quoted from references [6,7]

34 1. TERMINOLOGY AND SYMBOLS

35 Terminology and symbols for chemical thermodynamics, recommended by the
36 International Union of Pure and Applied Chemistry (IUPAC) through the Commission on
37 Physicochemical Symbols, Terminology and Units [8] and the Commission on
38 Thermodynamics [9] will be adopted here. For example, the usual symbols U , H , G , S ,
39 and C_p will be adopted for internal energy, enthalpy, Gibbs energy, entropy, and heat
40 capacity at constant pressure, respectively. A change in these thermodynamic quantities is
41 indicated by using the symbol Δ followed by a subscript (specifying the process to which
42 the quantity refers). For instance, a reaction Gibbs energy is represented by $\Delta_r G$, a
43 combustion enthalpy by $\Delta_c H$, a solution enthalpy by $\Delta_{\text{sol}} H$, a vaporization entropy by
44 $\Delta_{\text{vap}} S$, and so on. Standard states will be denoted by the superscript ‘ $^\circ$ ’, as in $\Delta_f H^\circ$ (H_2O ,
45 l), the standard enthalpy of formation of liquid water. No symbol has been approved by
46 IUPAC for ‘dissociation energy’ in the chemical thermodynamics section of reference 8.
47 Under “Atoms and Molecules”, either E_d or D is indicated. The latter is more common
48 and IUPAC recommends D_0 and D_e for the dissociation energy from the ground state and
49 from the potential minimum, respectively. We will use $D_{U,m}^\circ(T)$ for a molar bond
50 dissociation *internal energy* and $D_{H,m}^\circ(T)$ for a molar bond dissociation *enthalpy*, both at
51 a temperature T . (Often DU_T° and DH_T° are used in the literature but these symbols are
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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 physical dimensions defined below have the dimensions of either molar energy (usual units $\text{kJ}\cdot\text{mol}^{-1}$) or molecular energy (usual units electronvolt, eV, where 1 eV corresponds to $96.485\ 34\ \text{kJ}\cdot\text{mol}^{-1}$). Where specific terms are intended as molar quantities, they are identified as such by the subscript m."

1.1 Bond Dissociation Energies and Enthalpies

bond dissociation energy, $D_U^\circ(\text{A-B}, T)$

For a bond A–B in a molecule AB, where A and B can be atoms or groups of atoms, the standard internal energy of the gas phase reaction where the only event is the cleavage of that bond, at a given temperature:



Note 1. The relation between standard bond dissociation energy and enthalpy is given by

$$D_U^\circ(\text{A-B}, T) = D_H^\circ(\text{A-B}, T) - RT$$

Note 2. The symbol T will be omitted whenever the temperature refers to $T = 298.15\ \text{K}$. In this case, if molar quantities are used [1],

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

and

$$D_{H,m}^{\circ}(A-B) = \Delta_f H_m^{\circ}(A, g) + \Delta_f H_m^{\circ}(B, g) - \Delta_f H_m^{\circ}(AB, g)$$

bond dissociation enthalpy, $D_H^{\circ}(A-B, T)$

For a bond A-B in a molecule AB, where A and B can be atoms or groups of atoms, the standard enthalpy of the gas phase reaction where the only event is the cleavage of that bond, at a given temperature:



Note 1. Bearing in mind that a bond dissociation enthalpy is simply the standard enthalpy of a particular reaction, the relationship between two values of $D_H^{\circ}(A-B, T)$ at different temperatures is easily obtained as:

$$D_H^{\circ}(A-B, T) = D_H^{\circ}(A-B, 0 \text{ K}) + (H_T^{\circ} - H_0^{\circ})_A + (H_T^{\circ} - H_0^{\circ})_B - (H_T^{\circ} - H_0^{\circ})_{AB}$$

At $T = 298.15 \text{ K}$, $D_H^{\circ}(A-B) > D_H^{\circ}(A-B, 0 \text{ K})$, because the sum of the last three terms in this equation is positive.

Note 2. There are plenty of publications where the standard enthalpy of the above reaction is called ‘bond dissociation energy’, and abbreviated by BDE or by $D(A-B)$. However, this designation (as well as the symbols) can be misleading and the above nomenclature is preferred. In this connection, IUPAC recommends D_0 for the dissociation energy at $T = 0 \text{ K}$ [therefore, $D_0 = D_U^{\circ}(0 \text{ K}) = D_H^{\circ}(0 \text{ K})$] and D_e for the hypothetical dissociation energy from the potential minimum [8].

Note 3. The subscript ‘sln’ is used to distinguish solution from gas phase bond dissociation enthalpies. Thus, $D_{H,\text{sln}}^{\circ}(A-B, T)$ 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:



The relationship between $D_H^{\circ}(A-B)$ and $D_{H,\text{sln}}^{\circ}(A-B)$ is given by the following equation. (As usual, the symbol ‘ T ’ has been dropped to indicate that the temperature is 298.15 K). $\Delta_{\text{solv}} H^{\circ}$ is the standard enthalpy of solvation:

$$D_H^{\circ}(A-B) = D_{H,\text{sln}}^{\circ}(A-B) + \Delta_{\text{solv}} H^{\circ}(AB) - \Delta_{\text{solv}} H^{\circ}(A) - \Delta_{\text{solv}} H^{\circ}(B)$$

This equation indicates that $D_H^{\circ}(A-B) = D_{H,\text{sln}}^{\circ}(A-B)$ when the solvation terms cancel out.

1.2 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.

stepwise bond dissociation enthalpy, $D_{H_i}^\circ$ (A–B), where $i = 1, \dots, n$

For a bond A–B in a molecule AB_n , where A is an atom and B is an atom or a group of atoms, the standard enthalpy of the gas phase reaction where the each successive event is the cleavage of one bond, at a given temperature:



These reactions describe, respectively, the *first*, the *second*, ..., and the n^{th} *bond dissociation enthalpies* in the molecule AB_n

mean bond dissociation enthalpy, $\overline{D_H^\circ}$, $\langle D_H^\circ \rangle$ (The latter is adopted here.)

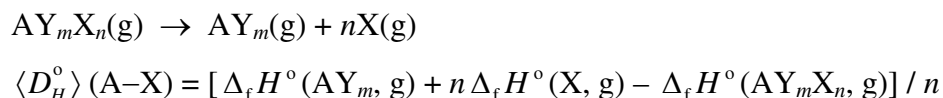
mean bond disruption enthalpy

For all bonds A–B in a molecule AB_n , where A is an atom and B is an atom or a group of atoms, the standard enthalpy of the gas phase reaction $\Delta_r H^\circ$, which represents the sum of the A–B bond dissociation enthalpies, at a given temperature:

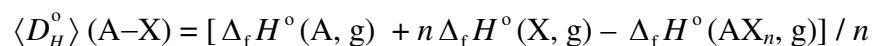


Note 1. The quantity $\Delta_r H^\circ / n$ represents the average enthalpy of cleavage of the A–B bond.

Note 2. The most general definition is as follows. For a bond A–X in a molecule AY_mX_n , where A is a central atom and X and Y are any mono- or polyatomic groups, $1/n$ times the enthalpy of reaction at $T = 298.15$ K:



Note 1. If A is bonded to a single type of ligand, as in AX_n , then



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 ($\Delta_{\text{at}} H^\circ$; see below) of methane, and

the mean bond dissociation enthalpy will be one quarter of this. The enthalpy of atomization of methane is $\Delta_{\text{at}}H^{\circ}(\text{CH}_4, \text{g}) = 1663.1 \text{ kJ}\cdot\text{mol}^{-1}$ and therefore the mean C–H bond dissociation enthalpy is $\langle D_H^{\circ} \rangle(\text{C–H}) = 415.78 \text{ kJ}\cdot\text{mol}^{-1}$. The stepwise C–H bond dissociation enthalpies are $D_{H_1}^{\circ}(\text{C–H}) = 435.14 \text{ kJ}\cdot\text{mol}^{-1}$, $D_{H_2}^{\circ}(\text{C–H}) = 444.50 \text{ kJ}\cdot\text{mol}^{-1}$, $D_{H_3}^{\circ}(\text{C–H}) = 444.50 \text{ kJ}\cdot\text{mol}^{-1}$ and $D_{H_4}^{\circ}(\text{C–H}) = 338.90 \text{ kJ}\cdot\text{mol}^{-1}$.

Note 2. Mean and stepwise bond dissociation enthalpies can also be defined in solution.

1.3 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 chemical bond strength. Consider the reaction where all the metal-ligand (M–L and M–X) bonds are cleaved simultaneously. The enthalpy of this disruption reaction at $T = 298.15 \text{ K}$ can be calculated by using enthalpy of formation data as a sum of n M–L and one M–X bond enthalpy contributions: .



$$\Delta_r H^{\circ} = nE(\text{M–L}) + E(\text{M–X})$$

The formal definition is:

bond enthalpy contribution, E

Note. Bond enthalpy contributions 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 [10,11].

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 is the basis to decide whether 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

[12]. 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 an 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 $E_s(\text{R–H})$, will therefore be given by the R–H bond dissociation enthalpy less the *reorganization energies* (E_R) of the fragments. To calculate $E_s(\text{R–H})$, 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.

1.4 Laidler terms

The so-called Laidler scheme has been developed as a tool to estimate standard enthalpies of formation of organic compounds [13]. 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 ($\Delta_{\text{at}}H^\circ$, 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 [14] and, more recently, by Leal [15]. 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 in the second part of this work, the Technical Report. Here we shall summarise the main quantities that are measured experimentally and lead to reaction enthalpy values.

2.1 Ionization energy and electron affinity

adiabatic ionization energy, $E_i(\text{AB})$

For any molecule AB (mono-, di-, or polyatomic), the minimum energy required to remove an electron from the isolated molecule at $T = 0$ K:



Note 1. The proviso $T = 0$ 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 reaction products do not interact, *i.e.*, they also conform to the perfect gas model.

Note 2. Equivalently, the adiabatic ionization energy is the standard internal energy or the standard enthalpy of the reaction at $T = 0$ K:

$$E_i(\text{AB}) = \Delta_r U_0^\circ = \Delta_r H_0^\circ$$

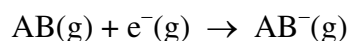
adiabatic electron affinity, $E_{\text{ea}}(\text{AB})$

For any molecule AB (mono-, di-, or polyatomic), the minimum energy required to remove an electron from the isolated anion at $T = 0$ K.

Note 1. Alternatively, the standard enthalpy of the reaction at $T = 0$ K:



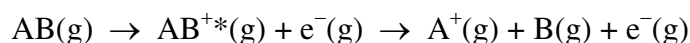
Note 2. This definition may appear somewhat counter-intuitive, since the word ‘affinity’ suggests that it should refer to the reverse process. That is why E_{ea} is often given as the negative of the enthalpy of the above reaction at $T = 0$ K [16]. The definitions are equivalent, and insure that, in most cases, electron affinities will have positive values; *i.e.*, the reaction is.



appearance energy (of an ion A^+), $A_{E_0}(\text{A}^+, 0 \text{ K})$

appearance potential (deprecated)

The standard enthalpy of reaction at $T = 0$ K for a diatomic or polyatomic molecule AB in the gas phase which, by means of an electron or a photon, is ionized and excited to a state AB^{+*} , which in turn subsequently decomposes into the fragments A^+ and B:



where A^+ and B are formed in their ground states and if these species and e^- have zero translational energies.

Note 1. It is obvious that, when reporting a value for an appearance energy, it is essential to state the parent molecule. Otherwise, one cannot identify the remaining species in the net reaction.

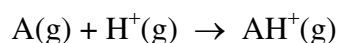
Note 2. The appearance energy is a widely used concept in threshold mass spectrometry experiments, which involve measuring the minimum energy required to cause a certain process.

proton affinity, basicity, and acidity

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

proton affinity, $E_{pa}(A)$

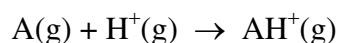
For any species A in the gas phase, the negative of the standard enthalpy of reaction at $T = 298.15$ K:



Note. The negative sign ensures that proton affinities have positive values.

gas phase basicity, $\Delta_{pba}G^{\circ}(A)$

For any species A , the standard Gibbs energy of reaction of proton to base attachment, usually at $T = 298.15$ K, for:



Note: Gas phase basicity is related to $E_{pa}(A)$ by:

$$\Delta_{pba}G^{\circ}(A) = -E_{pa}(A) - T[S^{\circ}(AH^+, g) - S^{\circ}(A, g) - S^{\circ}(H^+, g)]$$

gas phase acidity, $\Delta_{acd}G^{\circ}(AH)$

For any molecule AH , the standard Gibbs energy of acid dissociation reaction, usually at $T = 298.15$ K, for:



Note: The standard enthalpy of this reaction, $\Delta_{acd}H^{\circ}(AH)$, is equal to the proton affinity of the anion, $E_{pa}(A^-)$. This quantity can be related to $E_{pa}(A)$ by using the adiabatic ionization energy of AH and the adiabatic electron affinity of A [6].

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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 be 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.

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

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