Requirements for Thermochemical Data in the Lighting Community

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Z. Naturforsch. **63a,** 423 – 434 (2008); received April 21, 2008

This paper is dedicated to the memory of Klaus Hilpert.
Presented at the EUCHEM Conference on Molten Salts and Ionic Liquids, Hammamet, Tunisia, September 16 – 22, 2006.

The need for thermochemical data in the lighting industry is reviewed; these data are required not only in the research and development phase but also throughout the product life cycle. This review has lead to: a summary of commercially available integrated thermochemical databanks; a bibliography of thermodynamic databases available in electronic format; a list of collections of thermodynamic data that are highly valuable but not available in electronic format; a bibliography for chemical systems of specific interest to research into high intensity discharge lamps. The bibliographies will be of interest to those involved in molten salts and ionic liquids research as well as to those seeking information on alloys, oxide systems and nuclear materials. A review of the current state of ab initio calculations for the determination of thermochemical parameters is also included.

Key words: Thermochemical Data; Light Sources; Molten Salts; Phase Diagrams.

1. Introduction

Lighting is used daily throughout the world and is responsible for power consumption of around 2650 TWh per annum. This represents almost 19% of worldwide electricity production [1, 2]. Assuming that electricity represents 16% of the global energy used worldwide (typically 20% in western countries), lighting represents something like 3% of the annual energetic resources of humanity. In fact the electricity demand for lighting depends on the country. For example in France 12.5% of the electricity generated is used for lighting, in Germany 9% but in the USA this quantity attains 21% (this is equivalent to the global electricity production of France and Italy together) [3]. Developing countries like Tunisia spend 34% of their electricity for lighting while the equivalent value for Tanzania is 86%. In fact, every day approximately 30 billion light sources operate and about 10 billion light sources are produced each year. The lighting industry, with approximately 1% annual growth, is one of the fastest growing industrial sectors. However, there are many opportunities for enhancing not only the efficiency and reliability of lighting systems but also improving the quality of light as seen by the end user.

One way to exploit these opportunities is to resolve some of the issues related to molten salt chemistry that restrict the performance and lifetime of many light sources that operate at high temperatures. An example is the use of metal halide mixtures in high intensity discharge lamps to enhance the quality of the spectral output. These mixtures, however, interact with the walls of the arctubes (usually silica or ceramics) and give rise to reactions that are responsible for the main failure mechanism of these devices, i. e. corrosion.

Other examples of the synergy between light source research and molten salts are compact fluorescent lamp (CFL) development (amalgams, emitters, glasses, phosphors) and ultra-high pressure lamps for projection displays (glasses, movement of tungsten by oxygen- and halogen-containing species).

To overcome some of the problems encountered in the development of light sources it is necessary not only to have an understanding of the fundamental science associated with light generation but also the physical and chemical interactions of the various compo-

0932–0784 / 08 / 0700–0423 $ 06.00

nents within the light source. These interactions have a large influence on the characteristics and performance of the devices because of the high temperatures and long time scales involved. In a high intensity metal halide discharge lamp for example, a detailed knowledge of the chemical composition allows the viscosity, electrical conductivity, heat capacity and thermal conductivity of the plasma to be calculated. These parameters help determine convection within the arctube, lamp voltage, concentration of radiating and charged species and the temperature profile of the plasma, respectively. It is the latter that determines the arctube wall temperature and hence the failure mechanisms. To carry out these complex calculations it is essential to have an extensive database of thermochemical parameters.

Typically there is a need to calculate chemical compositions over wide ranges of temperature and pressure including gas-solid, gas-liquid and solid-liquid equilibria and complex gas mixtures containing charged species. The following assumptions have been made for the temperature and pressure ranges of interest to those involved in light source and lighting research and development:

temperature range:	200 to 8000 K,
pressure range:	1 to $2 \cdot 10^7$ Pa.

Timescales range from 10^{-6} s for atomic and molecular processes to 10^8 s for lamp life.

In addition to a large range of gaseous species, there are many mixtures that are of great importance to the science and technology of light sources. Examples include: glasses; ceramics; alloys; semiconductors; oxides; metal halide systems; amalgams. Thermochemical models representing the interactions are required to calculate the chemical composition of mixtures.

As part of the work carried out under COST Action 529, 'Efficient Lighting for the 21st Century' (http://www.efficient-lighting.org), a survey of thermochemical data for lighting research has been conducted. This has given rise to:

- a summary of commercially available integrated thermochemical databanks (ITDs);
- a bibliography of thermodynamic databases available in electronic format;
- a list of collections of thermodynamic data that are highly valuable but not available in electronic format;
- a recommended format for storing thermodynamic parameters of pure substances;
- a brief review of models available to represent interactions in mixtures.

Additionally, a number of bibliographies have been gathered which provide references to systems of specific interest to research into high intensity discharge lamps. Other sections of this paper briefly review the uses, advantages and limitations of experimental techniques for measuring properties of metal halides and metal halide mixtures and provide an overview of the use of ab initio methods to calculate thermodynamic data. These collections are of importance not only to those involved in research into the design, development and production of light sources but also to the wider community of molten salt and ionic liquid researchers.

Although the traditional use of thermochemical data is during the research and development stage, it is important to appreciate that data are also needed for each stage of the product lifecycle. For example, chemical modelling is often used to provide an understanding of production processes. Such understanding is then frequently used to provide process control. Similarly, the determination and control of the end of life mechanisms are usually established only with the aid of chemical modelling. Other applications include ensuring compliance with standards and regulations and the recycling, disposal and reuse phases of the product lifecycle.

2. Thermodynamic Data

To calculate chemical compositions the following parameters are needed for each species within the system of interest:

chemical formula and phase label;

standard enthalpy of formation at 298.15 K, $\Delta_f H°(298.15\ \mathrm{K})$;

standard entropy at 298.15 K, $S°(298.15\ \mathrm{K})$;

temperature variation of the heat capacity over the range of interest, $C_p°(T)$.

2.1. Reference States

For standard enthalpies of formation the reference states are the corresponding elements in their stable form, with natural isotopic mixtures, at 298.15 K and $p = p^\circ$, where p° is the standard pressure. By convention p° is taken to be 100000 Pa.

There is one exception to the above: for elemental phosphorus the reference state is white phosphorus, even though red phosphorus is the thermodynamically more stable form.

Thus for NaI, the standard enthalpies of formation are defined as the enthalpy changes for the following reactions:

$$\mathrm{Na}{<}\mathrm{s}{>} + 1/2\mathrm{I}_2{<}\mathrm{s}{>} = \mathrm{NaI}{<}\mathrm{s}{>}, \quad \Delta_\mathrm{f}H^\circ(\mathrm{NaI}, \mathrm{s}, 298.15\ \mathrm{K}), \tag{1}$$

$$\mathrm{Na}{<}\mathrm{s}{>} + 1/2\mathrm{I}_2{<}\mathrm{s}{>} = \mathrm{NaI}{<}\mathrm{l}{>}, \quad \Delta_\mathrm{f}H^\circ(\mathrm{NaI}, \mathrm{l}, 298.15\ \mathrm{K}), \tag{2}$$

$$\mathrm{Na}{<}\mathrm{s}{>} + 1/2\mathrm{I}_2{<}\mathrm{s}{>} = \mathrm{NaI}{<}\mathrm{g}{>}, \quad \Delta_\mathrm{f}H^\circ(\mathrm{NaI}, \mathrm{g}, 298.15\ \mathrm{K}), \tag{3}$$

where the phase labels are: <s> = solid; <l> = liquid; <g> = gas.

By definition the standard enthalpy of formation for an element in the reference state is 0. Values of S°(298.15 K) and $C_p{}^\circ(T)$ can be found in tabulations by CODATA [4] and SGTE (Scientific Group Thermodata Europe) [5]. Any thermodynamic database should be based upon and consistent with the CODATA key values for thermodynamics.

2.2. Thermodynamic Databases

Thermodynamic databases available electronically include:

SGTE pure substance database:
http://www.sgte.org;
FACT compound database:
http://www.factsage.com;
HSC: http://www.outokumputechnology.com/hsc;
TAPP: http://www.esm-software.com/tapp;
MALT2:
http://www.kagaku.com/malt/emalt2.html;
IVTANTHERMO:
http://www.openweb.ru/thermo/index_eng.htm;
NIST web book:
http://www.webbook.nist.gov;
NASA: http://www.grc.nasa.gov/www/ceaweb;
Kaye & Laby:
http://www.kayelaby.npl.co.uk.

Users must be aware that electronic databases have to be in a format compatible with the software being used to carry out the chemical composition calculations. It is important to note that different electronic formats of the same database do not always contain the same datasets.

Most thermochemical databases represent a critical evaluation of thermodynamic data and hence only one value is given for each parameter. In some cases these values are assigned uncertainties. These critical evaluations often involve a collection of experimental and theoretical values from many sources. These assessments are not usually available to the end user.

There are no thermochemical databases available that are dedicated to lighting. Proprietary databases are held by several companies and institutions involved in lighting research, development and manufacture.

2.3. Problems about Compatibility

For reliable and effective use, the data for any particular set of calculations must be assessed using consistent models and reference states. Otherwise the data for the individual subsystems will be inconsistent with each other and calculations using the combined data will give wrong results. Furthermore, because the demands of the industry are so varied and may require data for an unplanned combination of elements, it is very desirable that all data should be interconsistent.

There are two distinct problems which arise with respect to reference states. Firstly, different tabulations of data may use different reference states as a basis for their data, e. g. JANAF thermochemical tables, 3rd edition [6], provide data for the Gibbs energy of formation while the Barin and Knacke tables [7] provide data for the Gibbs energy relative to the pure elements at 298.15 K. Mixing data from these two different sources will, unless corrected, give results which are in error. Secondly, data for solution phases, e. g. alloys and slags, are based ultimately on data for the pure components in the particular phase. The difference in Gibbs energy between two phases for a particular element (sometimes called lattice stability) is a fundamental set of standard reference data upon which a critical assessment of data or a thermodynamic database is built. Datasets which use different data for these pure components cannot in general be mixed. For alloy systems this has been resolved to a large degree through an initiative taken by SGTE whereby data for the various crystalline and liquid phases of the most important elements were critically assessed and published [5]. These are now established as the standard world-wide, to the great benefit of all, and most particularly to SGTE members and licensees of databases, since their use adds to the volume of compatible assessed data for binary and higher-order systems.

Models also need to be defined in such a way that compatibility is promoted. There has been good progress on models and solution data for alloy systems. Standards are less well established for other solution phases, especially for systems in which the interactions between components within a phase are strong and charged species are involved. Of particular current interest are liquid oxides for which four different models are being used by NPL (UK), KTH Stockholm (Sweden), IRSID Metz (France) and Ecole Polytechnique Montreal (Canada). Another difficult area is that of concentrated aqueous solutions for which the models may need to cover many types of solute and extend to high temperatures and pressures as well as cases in which water is a minor component. From one perspective the multiplicity of models is unfortunate because the systems are difficult to model and the effort is multiplied. On the other hand it is desirable on balance for competing models to be developed so that the most useful can be established by peer evaluation and their effectiveness when applied to practical problems. Organisations such as CALPHAD [8, 9] serve to encourage discussion on the applicability of models for various types of phases. More recently workshops have been held specifically to obtain broad consensus on models and data suitable for use over the next 20 years [10, 11]. Such ventures need to be encouraged.

2.4. International Collaboration

Ideally the effort needed to generate the large base of data required to tackle unanticipated problems should be undertaken in the context of international co-operation. In practice there is no possibility of the common funding that would encourage the adoption of common standards and the contribution of CODATA [4, 12], though useful, is minor. Nevertheless, it is normal practice for research on models to be freely published. On the other hand data using those models are often published only selectively or in full after a significant time has elapsed, either because they were developed for a particular application or because of their value as part of a commercial database.

The cost per beneficiary can be reduced when projects are jointly funded like that on pyrometallurgical extraction [13]. Various types of consortia such as SGTE have arisen to enable a limited cooperation to be established within a framework of rules. COST 507 (light alloys) is an example of an European project in which each country bears its own costs but all share in the benefits. The disadvantage of such groups is that the participants may be inhibited from enjoying the benefits of cooperation with or working for third parties. The international organization CALPHAD, which runs a journal and whose participants have no formal agreement with each other but can get together at the annual meeting, has been very successful in advancing the methodology, raising standards through peer pressure and stimulating the flow of published data without these disadvantages. The Journal of Phase Equilibria also plays a valuable role in publishing compilations and assessments with a standard format. The Alloy Phase Diagram International Commission (APDIC) [14] is helping to coordinate effort on alloy systems world-wide. In the UK awareness and some degree of coordination is fostered by the Materials Chemistry Committee of the Institute of Materials.

2.5. Availability of Experimental Data

The period 1950 to 1970 was one where experimental methods were able to produce good quality results, and much useful work was published. Unfortunately, since then there have been relatively few experimental studies on basic systems for two reasons:

a. Experimental thermodynamic and phase equilibrium studies became less fashionable, especially as techniques for microstructural and kinetic studies blossomed. The provision of data was seen to be unoriginal and incompatible with study for a higher degree.

b. The trend was established to target research funds to applied ends, and it became difficult to justify the funding of experimental thermodynamics because of the effort and timescales required.

The result has been that, even though many experimental data have been published but not yet critically assessed, there are now gaps in published experimental work relevant to important applications. Moreover, there has been a very great decline in the number of experimental facilities and the maintenance of those that are left so that, when the need arises for experimental data to fill a gap, no suitable equipment and associated expertise can be found.

2.6. Sources of Thermodynamic and Phase Diagram Data

Compilations of thermodynamic and phase diagram data are essential. In this section the various types of sources of data are identified and some indication is given of their relative strengths and weaknesses.

Ultimately nearly all data that are used originate from a journal or a report that is, in principle, publicly available. A literature search could be carried using the standard abstract services for relevant documents. This task has been made easier by use of publications such as those by Wisniak [15], Cheynet [16] and Prince [17, 18] and equivalent computer-based products [19] which provide a list of references for the thermodynamic and phase diagram information for a particular system but with no attempt to analyze or report the information given. The series of volumes “Phase Diagrams for Ceramists” [20] provide further information concerning phase diagrams of oxide, sulfide and salt systems. Generally this information is abstracted from published papers and not critically assessed through comparison with other information on the same system. For alloy systems this service is also provided by the Ageev series [21] also occasionally known as the ‘Red Book’. They nevertheless provide a vital source of information.

The next most important sources of data are the standard critically assessed publications. These include the JANAF [6, 22], Barin et al. [7, 23], NBS Tables of Chemical Thermodynamic Properties [24, 25], Medvedev et al. [26], IVTAN [27 – 32], SGTE compilation [33], Kubaschewski et al. [34], Barin [35], Knacke et al. tables [36] for thermodynamic properties.

Separate data sources are available for nuclear materials [37, 38] and sulfides [39]. The US Geological Survey has also provided data for mineralogical systems [40].

Various sources of critically assessed phase diagram information are available. These include: alloy systems [41 – 54], oxide systems [55], binary halide systems [56]. Certain compilations provide both thermodynamic and phase diagram information [57, 58] for a number of alloy systems.

The series of monographs published by ASM [59 – 62] provide a review of the thermodynamic information for selected binary systems as well as phase diagram information.

The CALPHAD journal and the Journal of Phase Equilibria also provide excellent reviews of data for various systems and often publish critically assessed data which can be used for the calculation of phase equilibria.

The IAEA monographs are an excellent source of information for nuclear-related systems [63 – 72].

3. Binary Metal Halide Systems

The chemical modelling of the multi-component metal halide systems used in high intensity discharge lamps is built upon thermodynamic descriptions of the corresponding binary mixtures. References [20, 56] and [73 – 78] describe collections of thermodynamic data for binary metal halide systems.

4. Bibliography of Published Data for Alkali Iodide-Lanthanoide Triiodide Systems

The alkali iodide-lanthanoide triiodide systems are of particular interest to the design and development of high intensity discharge lamps. A bibliography of published articles describing the properties of these systems is provided in [79 – 102].

5. Experimental Methods Used in the Determination of Thermochemical Parameters

The thermodynamic key data, which are used as a basis for building up databases have to be determined by experimental techniques. As described above, the key parameters are enthalpies and entropies of formation, as well as heat capacity data and for mixtures, enthalpies of mixing and Gibbs energies. They can either be measured directly or determined while using conversions from other experimentally derived values. Also for the assessment and optimization of solutions, thermodynamic data from various kinds of experiments can be used. This section will give a short overview of some of the available experimental techniques without claiming completeness. A description of the derivation of thermodynamic parameters for modelling metal halide discharge lamps is provided in [103]. General texts covering some important aspects of the experimental methods used in the measurement of thermochemical properties are provided in [104, 105].

5.1. Principles and Methods of Calorimetry

Calorimetry is the measurement of the heat absorbed or generated in a substance under study as it undergoes a change from a well defined initial state to a well defined final state. This change may result from chemical reaction, dissolution or dilution, or a physical change such as vaporization, sublimation or melting. It may also result from the changes in temperature and other thermodynamic variables such as pressure, magnetic- and electric field. There are many different kinds and methods of calorimetry, the most important ones for determining data of interest to lighting are described below. Some aspects of high temperature calorimetry have been summarized by Navrotsky [106].

5.2. Differential Scanning Calorimetry (DSC)

If a sample and the corresponding reference are heated at the same rate, the heating powers required are proportional to their respective heat capacities. The heat capacity of the sample is determined from the heating power and the base line and also sensitivity calibrations. Enthalpies of transitions are determined by integration of the peak in the power versus time curve corresponding to the transition. In temperature-modulated DSC, a sinusoidal temperature change is superimposed on the constant heating rate. From the amplitude and phase of the modulated DSC power, the heat capacity is obtained.

5.3. Reaction Calorimetry

Measurements of enthalpies of mixing, dissolution and general chemical reactions belong to the reaction calorimetry. Enthalpies of combustion are measured in bomb calorimeters based on an adiabatic principle. General reaction calorimetry includes the measurements of molten salt systems and metallic systems.

5.4. Drop Calorimetry

To measure enthalpies, a sample at room temperature, T_0, is dropped into an empty platinum crucible of temperature T. In this way, one can measure the heat content of the sample, when neither reaction nor transformation of the sample occurs in the calorimeter. This drop calorimetric method can be applied to the sample that transforms to another phase or reacts with gas in the calorimeter within a limited time, typically about 30 minutes.

5.5. Calvet Calorimeter

This twin calorimeter to measure the heat flux was originally designed by A. Tian and E. Calvet. This type of microcalorimeter is widely used to measure a small heat effect at high temperatures. The calorimeter has two sample chambers in symmetrical positions in a massive metal block which works as a heat sink. Several furnaces outside the block maintain a constant uniform temperature. Several tens of thermocouples are placed between each cell and the block. The reaction takes place in one cell while the other cell acts as a reference. The heat generated by the reaction is transferred to the block through the thermopile. When the temperature gradient between the cell and the block is small, the rate of heat flow between them is proportional to the temperature differences.

5.6. Differential Thermal Analysis (DTA)

In DTA the difference in temperature between the sample and an inert reference, ΔT, is measured while both are subjected to the same heating or cooling program. Transition temperatures and the associated enthalpy changes are measured using this technique.

5.7. Thermogravimetric Analysis (TGA)

TGA is one of the most popular techniques of thermal analysis, in which the change of sample mass under a programmed temperature change is recorded as a function of temperature and/or time. Various physical and chemical processes accompanying mass change are subjected to the measurements. The method gives useful information about thermal stability of the material, reaction pathway, kinetics of reaction, quantity of a specific component and so on.

5.8. Knudsen Effusion Mass Spectrometry (KEMS)

High temperature mass spectrometry is the most important method for the analysis of vapours over condensed phases in order to determine thermodynamic data. Many condensed phases have been studied by this method and their thermodynamic data have been determined. The thermodynamic data result from the measured temperature dependence of the partial pressures of the identified gaseous species. A special variant of this technique, which is frequently used in inorganic gas phase chemistry, is KEMS. Vaporization studies in the range between room temperature and temperatures above 2500 K can be carried out by this method, and thermodynamic data can be determined. The dissociation energies of a large number of gaseous species have been obtained by this method. Investigations by KEMS generally mean the study of equilibrium reactions involving neutral molecules and/or atoms. The potential of the KEMS technique for the use in the course of high temperature chemistry can be summarized as follows:

a. identification of the equilibrium gaseous species of the vapour in the Knudsen cell;

b. partial pressure determination of the equilibrium species, generally in the range between 10^{-5} Pa and 10 Pa and up to temperatures of more than 2500 K;

c. computation of thermodynamic properties by using the determined temperature dependence for enthalpies and entropies of vapourization, dissociation and formation or the temperature dependence of equilibrium constants of chemical reactions.

Detailed accounts of the theory and techniques used in KEMS are contained in [107 – 110].

5.9. Other Mass Spectrometric Techniques

Other mass spectrometric methods used for determination of thermodynamic data of high temperature inorganic vapours are transpiration mass spectrometry (TMS) and laser-induced mass spectrometry (LVMS). For LVMS the vapourization coefficient must be known if equilibrium vapour pressures are to be obtained, in contrast to KEMS and TMS. The principle of TMS is that the equilibrium to be investigated is present in a transpiration reactor. The operation, flow velocity of carrier gas and the construction (diffusion barriers) of the transpiration reactor should enable the establishment of thermodynamic equilibrium in the reactor. A molecular beam sampling mass spectrometer enables the analysis of condensable species in the high temperature gas stream from the transpiration reactor.

5.10. Electromotive Force (EMF)

When a suitable galvanic cell is constructed, the Gibbs free energy change of the cell reaction can be derived from the measurement of EMF of the cell. Thermodynamic properties of the material can be obtained based on the relation between the physical meaning of the cell reaction and the EMF measured.

5.11. Spectroscopic Methods

The most widely employed spectroscopic methods are: Raman spectroscopy for determining vibrational frequencies and the structure of gaseous molecules; infrared spectroscopy for determining vibrational and rotational frequencies of gaseous molecules; ultraviolet spectroscopy for determining electronic structures.

Electron diffraction is used to provide bond angles and bond lengths of gaseous species.

6. Comments on ab initio Calculations for Thermochemical Parameters

Computational chemistry covers a range of techniques from ab initio quantum mechanics to classical molecular mechanics and dynamics. This discussion will be restricted to the more fundamental ab initio methods that, in principle, allow the calculation of thermodynamic properties of ideal gaseous species of relevance to light sources research. The aim here is not to go into any great depth but to give an overview of what can and cannot be currently achieved.

In this context ab initio method means a fundamental method for the calculation of both the energy and structure of a molecule where a minimum of input information is required. Ideally this would be limited to an indication of the nature of the atoms and their relative proportions in the molecule under study. In practice additional information such as a description of the atomic wave functions (basis sets) and some ‘guess’ at the structure are required (multiple minima in the energy representing alternative molecular structural forms are common). A second source of uncertainty comes from the very nature of the calculation which must be done – the solution of the Schrödinger equation. This can be thought of as a multibody (electrons and nuclei) interaction problem and although the fundamental physics of the electromagnetic interactions that must be accounted for are understood, the multibody aspect means that only an approximate numerical solution can be obtained. In principle more and more accurate solutions are possible, however, they can become computationally very expensive and much research recently has focussed on doing this in the most efficient ways possible.

The required thermodynamic properties are $\Delta_f H^\circ(298.15\text{ K})$, $S^\circ(298.15\text{ K})$ and $C_p{}^\circ(T)$. From these properties of an ideal gas species it is possible to calculate the Gibbs energy of the species at any temperature within the range of validity of the C_p function. Traditionally the problem of calculating (usually called ‘estimating’) the value of $\Delta_f H^\circ(298.15\text{ K})$ of a gaseous molecule was tackled using one of many bond energy estimation schemes commonly used in organic chemistry [111]. To some extent the 'force fields' of modern molecular mechanics and dynamics are a more sophisticated version of the traditional bond energy estimation scheme.

6.1. The Enthalpy Problem

The most basic of ab initio calculation is a single point energy calculation. This takes a given molecular structure (nuclei positions) and determines the total energy by optimally distributing the electrons by the calculation of molecular orbitals and electron distributions. Although this calculation can often be performed to very high accuracy the energy obtained is for the process:

$$\mathrm{MX}\langle g\rangle = \mathrm{M}^{n+}+\langle g\rangle + \mathrm{X}^{y+}\langle g\rangle + (n+y)\mathrm{e}^{-}\langle g\rangle, \quad (4)$$

where all the nuclei and electrons are separated at 0 K.

This means that for a calculation of, say, the association enthalpy of 2 NaI<g> to form Na_2I_2<g> two separate calculations (for NaI and Na_2I_2) must be done producing two very similar total energy values which must then be subtracted to yield the desired result. This clearly places a very high accuracy requirement on the two independently calculated energies. For example calculations [112] on Na_2I_2<g> and 2 NaI<g> yield total enthalpies (relative to nuclei and electrons) of -912687.550 and -912528.469 kJ·mol^{-1}, respectively, at 298.15 K. From these values the predicted association enthalpy is -159.1 kJ·mol^{-1} (compared to the SGTE substance database value of -175.6 kJ·mol^{-1}). Although the agreement in normal thermochemical terms would not be considered good, this result actually shows that ab initio calculation of total enthalpy is accurate to less than 0.002%.

6.2. Thermal Functions – Heat Capacity and Entropy

Entropy (S) and heat capacity (C_p) may be estimated from the standard equations of statistical mechanics [6, 27] together with the molecular mass, moments of inertia (i. e. molecular structure) and values of various vibrational and electronic energy levels. The energy in a molecule may be considered to be partitioned between translational, rotational, vibrational and electronic states. For all practical purposes translational energy levels may be considered continuous, and the only requirement is to know the mass of the molecule. In a similar way, for most molecules of concern to lighting research, the rotational energy levels can also be approximated as continuous and the molecular structure (to allow moments of inertia to be calculated) is all that is required.

Such simplifications cannot be made when considering the vibrational contributions to S and C_p. The energies of the $3N-6$ ($3N-5$ for a linear molecule) vibrational modes of a molecule, containing N atoms, need to be determined. For the highest accuracy calculations corrections for anharmonicity, in the vibrational modes, should be made but in general this will not be possible. An additional complication is that errors may also be introduced by considering all of these modes as corresponding to vibrations or torsions when in reality internal rotation (free or hindered) is present.

A successful ab inito calculation on a molecule will result in the accurate prediction of its structure (bond distances and angles); this in turn may be used to calculate the rotational entropy contribution via the moments of inertia. From a structure, at an energy minimum, most computational chemistry codes will allow the calculation of the frequencies of the vibrational modes of the molecule and hence the vibrational contribution to the heat capacity and entropy. In principle ab initio calculations can also determine the energy and structure of a non-ground state and hence provide information about the electronic excitation of the molecule.

6.3. Types of Method

Although all methods attempt to solve the Schrödinger equation by numerical approximations there appears to be broad division between Hartree-Fock-based and density function theory (DFT) approaches. It is also possible to combine different methods using difference basis sets and levels of theory, and these composite methods, mainly developed for atoms lighter than argon, give results of the highest accuracy. Even for on-composite methods, one method may be used to calculate the molecular structure and another the energy of that structure. The tendency is to use a computationally 'cheap' method for structure and one with a more involved level of theory and perhaps complex basis set for the energy. If choosing a single method then DFT appears a reasonable choice.

In addition to the method of solving the Schrödinger equation a set of basis wave functions must also be chosen. Unfortunately there are a limited number of readily available basis sets that cover a wide range of atoms heavier than argon. This is partly because of the difficulty in deriving high quality basis sets for large atoms but also because of the historical focus of computational chemistry on organic molecules. Fortunately effective core potential-based basis sets such as SDD (Stuttgart/Dresden) have a very wide coverage of atoms.

6.4. Limitations and Problems

Monatomic molecules are not usually considered by most general purpose ab initio codes as the thermodynamic properties are dependent only on the atomic (electronic) energy levels. These are most likely known better than the basis set atomic wave functions that are the fundamental basis of the ab initio calculation.

The limitation on the size of molecules is usually in terms on the size and number of atoms – essentially the number of electrons and the number of functions comprising the basis set. Basis sets for very heavy atoms can be simplified by treating the inner, more tightly bound, electrons as a single entity. The detail is then put into the outer electrons more likely to be involved in forming bonds. For example atoms up to argon in the periodic system of the elements have a large number of basis sets readily available, however, for an atom such as iodine, one usually has to rely on effective core potential basis sets. The optimization of the molecular structure will not necessarily determine the global minimum in energy of the molecule but may converge to a local minimum depending on the starting structure. This is partly a problem but also does give the ability to perform calculations of isomers. A more significant problem may be convergence failure if the optimization algorithm is very sensitive to the starting structure.

6.5. Software

It is not possible to discuss the merits of the various software implementations of the calculations described above. However, there is a wide range available, either as full commercial products, or freeware. Invariably the differences are more related to usability and range of methods available rather than the quality of results obtainable.

Acknowledgements

This work was initiated and funded by COST 529, ‘Efficient Lighting for the 21st Century’.

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