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THEORETICAL METHODS IN THERMODYNAMICS OF CONDENSED PHASES

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Abstract

Theoretical possibilities of determining energetic and thermodynamic characteristics of chemical entities in gaseous and condensed (solid and liquid) phases are briefly reviewed. The considerations include quantum chemistry methods which enable evaluation of energetic quantities and statistical thermodynamics dependencies necessary for determining other thermodynamic characteristics. The possible applications of these methods are also discussed in brief.

Keywords: chemical systems, energetics, theory of, thermodynamics

Introduction

The structure of chemical entities in minimum energy stationary states can be established absolutely by diffraction methods, i.e. X-ray, electronography or neutronography [1, 2]. In addition, numerous spectroscopies such as IR, NMR, EPR, electronic absorption and emission or photoelectron provide indirect information on this matter [1, 3]. On the other hand, calorimetry, thermoanalytical techniques, as well as spectroscopic and electrochemical methods enable determination of thermodynamic characteristics of the systems in certain states (lowest energy or free energy and equilibrium states) [1, 4, 5]. Using experimental techniques we are, however, unable to disclose the structure and thermodynamic quantities of molecules or conglomerates of these in stationary transition states (saddle points) – with the exception of energetic characteristics which can sometimes be extracted from kinetic measurements.

Theoretical methods enable prediction of the structure of chemical entities in stationary states corresponding to both energy minima and saddle points [6, 7]. Moreover, complete energetic and thermodynamic descriptions of molecules in these states is possible combining quantum chemistry [6, 7] or density functional theory [8] methods with statistical thermodynamics [9]. This permits determination of energy difference between saddle points and relevant energy minima – which reflect activation barriers, and create a basis for theoretical examination of kinetics of chemical processes [10, 11]. Application of quantum

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mechanics and density functional theory also enables us to gain quantitative information on numerous properties of molecules such as polarity (dipole moment), polarizability, as well as electron detachment (ionization potential) or attachment (electron affinity) ability [6, 8]. Furthermore, the above mentioned methods provide partial charges on atoms and predict distribution of electrostatic potential around the molecules. The latter information is crucial in understanding the behaviour of chemical entities in condensed phases and, among others, in living matter [12].

Theoretical methods found wide application for describing gaseous systems in which molecules can be treated as isolated species not interacting with each other. In condensed phases, molecules interact with the surroundings or, in other words, are influenced by the potential of the surroundings (in gaseous phases this potential is usually negligible). The inclusion of these interactions provides information on the structure and thermodynamics of condensed phases. The latter problem is the main issue of this brief review.

Energetics and thermodynamics of gaseous systems

According to the quantum mechanics, the energy and other related properties of molecules may be obtained by solving the Schrödinger equation:

$$\hat{H}\Psi = \mathrm{E}\Psi \tag{1}$$

where Ψ is the wavefunction and $\hat{H}$ the energy (E) operator (Hamiltonian) [1, 6, 7]. For most of molecular systems it is justified to assume that the nuclei remain stationary and only electrons continue in motion. This approximation (known as the Born-Oppenheimer approximation) boils down the problem to solving the Schrödinger equation for the electrons (el) alone

$$\hat{H}_{\mathrm{el}}\Psi_{\mathrm{el}}(r,R) = \mathrm{E}_{\mathrm{el}}(R)\Psi_{\mathrm{el}}(r,R) \tag{2}$$

where r denotes electron and R-nuclear coordinates. It results from this approximation that the energy depends on the structure of molecules. Hamiltonian for isolated molecules combines two terms

$$\hat{H} = \hat{T} + \hat{V} \tag{3}$$

i.e. kinetic (reflecting motions of electrons) $\hat{T}$ and potential (reflecting all types of electrostatic interactions) $\hat{V}$ energy. The electronic wavefunction in Eq. (2) is a combination of molecular spin orbitals (constructed according to the Hartree-Fock scheme [6, 7] extended by Roothaan and Hall [13, 14]) of which each is a linear combination of so-called basis functions (basis sets) (coefficients of the latter expansion are optimized by the Self-Consistent Field (SCF) procedure). The name ab initio refers to complete calculations performed solely on the laws of quantum mechanics in different basis sets [6, 7]. Semi-empirical methods use parameters derived from experimental data (enthalpies of formation, ionization potentials, spectral characteristics) to simplify the computations [6, 7, 15, 16]. In the density functional theory, the expression for the energy and for an electronic wavefunction include terms accounting for the exchange energy (resulting from the quantum nature of the electrons) and for the electron correlation (arising from electrons interacting with one another) [8].

As a result of quantum mechanical calculations, energies (E) and geometries of molecules are obtained. Having energies for all entities occurring in the equation defining formation of a given compound one can determine the energy of its formation ($\Delta_f E$) on the basis of Hess's Law [1, 6, 7]

$$\Delta_f E = (E_{\text{molecule}})_g - \sum_e n_e[(E_{\text{elements}})_g]_e \tag{4}$$

where n_e denotes stoichiometric coefficients of all elements (e) (in a stable form in a gaseous phase). The standard enthalpies of formation ($\Delta_{f,T}H^0$) of compounds in the gaseous phase can be obtained adding the zero point energy term (ΔE_0), and the terms accounting for the heat capacity changes ($\int_0^T \Delta C_p^0 dT$) and changes of enthalpies of elements resulting from transfer between gaseous and standard state in the usual sense (pressure=1 atm at a given temperature (T)) ($\Delta H_{\text{elements}}$) [1]

$$\Delta_{f,T} H^0 = \Delta_f E + \Delta E_0 + \int_0^T \Delta C_p^0 dT - \Delta H_{\text{elements}} \tag{5}$$

Zero point energy (E_0) contribution for a given entity can be derived using the equation [1, 6, 7]

$$E_0 = \frac{1}{2} Nhc \sum_k \bar{\nu}_k \tag{6}$$

in which N, h and c denote the Avogadro number, Planck constant and velocity of light, while $\bar{\nu}$ – the wavenumber of a normal mode in the molecule (summation extends over all molecular vibrations (k)). Multiplication of E_0 values thus obtained by relevant stoichiometric factors and summation analogous as in Eq. (4) gives the values of the ΔE_0.

Values of $\int_0^T \Delta C_p^0 \, \mathrm{d}T$ can be evaluated on the basis of the statistical thermodynamics [9]. Finally, values of $\Delta H_{\mathrm{elements}}$ are most often assumed on the basis of experimental heats of volatilization of elements.

Predicted, in the above described manner, enthalpies of formation strongly depend on the size and features of the basis sets used. Often, only relatively large basis sets with included electron correlation provide values which are comparable to the experimental ones [7, 17]. This, however, requires time consuming calculations. It has also been noted, that energetics of small (diatomic) molecules is usually poorly reflected by quantum chemistry methods. If such molecules are the substrates in the reaction of formation of a given compound, their energies influence the energies and enthalpies of formation. To avoid such an effect the introduction of a so-called isogyric [18] (or higher order [19]) correction, whose magnitude is given by the difference between experimental and theoretical (on the level of a certain basis of functions) dissociation energies of diatomic molecules divided by 2 and multiplied by a total number of unpaired electrons in all monoatomic species constituting a given entity, has been proposed. This type of corrections has been included in G1 [20] and G2 [19] theories which combine various quantum chemistry methods in such a way as to obtain the most reliable values of heats of formation in a reasonable time of calculation. Another approach, sound in the case of medium size molecules, combines theoretical heats of hydrogenation with enthalpies of formation or reaction products – if the latter characteristics are established accurately enough, either experimentally or theoretically [21]. Thermochemistry of larger compounds is considered in the category of so-called isodesmic reactions in which the number of each kind of formal chemical bond is conserved [22, 23].

Semi-empirical methods, such as MNDO [24], AM1 [25] or PM3 [26] provide enthalpies of formation at a chosen temperature [15], which is achieved by the use of an approximate form of the Schrödinger equation supplemented with parameters of an experimental origin [7].

Finally, the enthalpies of formation of relatively large species can be predicted utilizing additive thermochemical models [21] such as Benson's group additivity method [27].

Energetics and thermodynamics of solid systems

Energetics of condensed phases can be described on the basis of quantum mechanics by extending the Hamiltonian for isolated entity (Eq. (3)) of the term ($\hat{H}_f$) reflecting the potential energy of a molecule as a result of interactions with the surrounding [6, 7]

$$\hat{H}_{\text{condensed phase}} = \hat{H} + \hat{H}_f \tag{7}$$

In the case of a solid phase, such an approach did not, however, find practical application in the examination of thermodynamics of solid phases. Instead, for theoretical description of energetics of ordered crystalline systems the approach proposed assumes that fragments constituting such a phase, whose energy can be determined by quantum chemistry methods, interact with each other and the energy of this interaction is reflected by the crystal lattice energy (E_c). The latter quantity is related to the amount of energy which has to be supplied to transfer molecules (A_nB_m) from the solid (s) to the gaseous (g) phase [1, 28]

$$(A_nB_m)_s \rightarrow (A_nB_m)_g(nA^{\alpha m+} + mB^{\alpha n-})_g \tag{8}$$

(in the case of molecular crystals, molecules are transferred unchanged, while ionic crystals – the hypothetical transfer concerns $A^{\alpha m+}$ and $B^{\alpha n-}$ ions (α is the multiplicator indicating actual valence of both ions)), i.e. with the equation

$$\Delta_f E\,[(A_nB_m)_g(nA^{\alpha m+} + mB^{\alpha n-})_g] - \Delta_f E[(A_nB_m)_s] = -E_c \tag{9}$$

In the theoretical description of the crystal lattice energy four contributions are considered, namely reflecting electrostatic (E_{el}), dispersive (E_d) and repulsive (E_r) interactions, as well as the term zero point energy (E_0) [28–31]

$$E_c = E_{el} + E_d + E_r + (E_0)_s \tag{10}$$

(the right hand side of Eq. (10) describes energy of interaction and is thus always negative which necessitates multiplication of the E_c value by –1 to enable its comparison with the left hand side of Eq. (9)). The electrostatic, dispersive and repulsive interactions are represented by the general equation

$$E_{el(d,r)} = \frac{1}{2}\,N\sum_{i}\sum_{i\neq j}\beta\left(\frac{P_iP_j}{R_{ij}^{a}}\right) \tag{11}$$

in which β is a factor equal to $1/(4\pi\varepsilon_0)$ (ε_0 is the permittivity of free space) for electrostatic and 1 – for dispersive and repulsive interactions, P denotes partial charge on an atom (if it concerns electrostatic interactions) or parameter ascribed to the atom (if is related to dispersive and repulsive interactions), R is the distance between the atom of a chosen molecule (i) and the atom of a molecule from the surrounding (j), while a equals 1 for electrostatic, 6 – dispersive and 12 – repulsive interactions. Repulsive interactions are often expressed by the exponential type dependency (the so called Buckingham potential)

$$E_r = \frac{1}{2} N \sum_{i} \sum_{i \neq j} C_i C_j \exp(-P'_i P'_j R_{ij}) \qquad (12)$$

(C and P' are the parameters characteristic of the pair of atoms). Finally, the term zero point energy in relation to the crystal lattice energy is given by the equation analogous to (6), in which the wavenumber refers to normal lattice mode ($\bar{\nu}_L$) and summation extends over L lattice vibrations [29, 30].

Crystal lattice energy can be calculated if the crystal structure, partial charges and parameters characterizing atoms are known. Having crystal lattice energies, the energies of formation of solid compounds at 0 K can be determined by Eq. (9). The energies of formation of gaseous molecules, necessary for carrying out the latter calculations, can be obtained employing quantum chemistry methods [6, 7]. The above described procedure therefore enables purely theoretical determination of energetic characteristics of crystalline phases. Further insight into the thermodynamics of solid phases is possible employing statistical thermodynamics, which enables determination of contributions to energy, enthalpy, entropy, free energy and free enthalpy resulting from the increase of temperature above 0 K [9]. To obtain the latter characteristics it is necessary to assume that the molecule is rigid, that all vibrations are harmonic and that temperature does not influence the dimensions of the unit cell and lattice vibrations. Despite these simplifications the thermodynamic characteristics derived by us [32–37] and others [30, 31, 38–40] correspond quite well to those originating from the experiment. Moreover, in several cases unknown characteristics could be predicted on this way [35–37].

Energetics and thermodynamics of liquid systems

Liquid phases – contrary to crystalline (perfectly ordered) and gaseous (perfectly disordered) ones, are only partially ordered. It is, therefore, difficult to describe energetic and entropic changes in such systems. The models which will be mentioned here were developed to describe thermodynamics of solutions.

Energetics of molecules dissolved in the liquid phase is reasonably well described by the Self-Consistent Reaction Field (SCRF) theory [7, 41, 42] which incorporates the Onsager reaction field model [43]. In this theory, the solvent is viewed as a continuous medium of uniform dielectric constant (ε), surrounding a spherical cavity of radium b_0 occupied by a molecule. It is assumed that a dipole in the molecule (μ) induces a dipole in the medium, and that the electric field arising from the solvent dipole in turn interacts with the molecular dipole. This leads to the net stabilization of the system. The interactions can, therefore, be considered in the category of electrostatic effect represented by an additional term $\hat{H}_f$ in the Hamiltonian (Eq. (7).

$$\hat{H}_f = \hat{\mu} \frac{2(\varepsilon-1)}{2\varepsilon+2} b_0^3 \mu \tag{13}$$

where $\hat{\mu}$ is the molecular dipole operator. As the dielectric constant and cavity radius are not predictable theoretically, the application of the SCRF model necessitates the respective use of experimental and assumed values of both quantities. It has been shown that despite some limitations of the SCRF theory (it does not apply to non-polar systems and requires the above-mentioned assumptions) it foresees energetics and some other features reasonably well (e.g. frequencies of molecular vibrations) of solute molecules immersed in the solvent [41, 42].

A more advanced approach was proposed by Cramer and Truhlar [44, 45]. According to this, the heat of formation ($\Delta_f H_{soln}$) of dissolved molecules (solute) is the sum of three contributions,

$$\Delta_f H_{soln}[\text{solute}] = \Delta_f H_g[\text{solute}] + E_{Coul} + E_{disr} \tag{14}$$

namely, the heat of formation of a solute in the gaseous phase ($\Delta_f H_g$[solute]), the energy of Coulombic interactions of solute and solvent (E_{Coul}) and the energy change which accounts for the disruption of the solvent structure due to the solute (E_{disr}), respectively. In these methods the Hamiltonian for isolated solute molecule, relevant to the semi-empirical MNDO [24], AM1 [25] and PM3 [26] methods, is modified (Eq. (7) so as to include solute-solvent interactions and changes in the constitution of a solvent upon formation of a solution. The subsequent parameterization, specific for a given solvent, enables determination of heats of formation on a solute in the liquid phase. This approach in somewhat modified form can be used for prediction of free enthalpies (energies) of formation, if parameterization is based on experimental values of the quantity. The Cramer-Truhlar scheme was originally incorporated into AM1 (SM1, SM1a and SM2 models) and PM3 (SM3 model) methods – with parameterization for water [44, 45]. This approach can, however, be included into more advanced semi-empirical or even ab initio methods (SPARTAN 3.1 program [46]). It is perhaps also worth mentioning on simplified Cramer-Truhlar schemes parameterized for water (aq) and hexadecane (hd) as solvents, incorporated into MNDO, AM1 and PM3 methods, and known under the names MNDO_{aq}, MNDO_{hd}, AM1_{aq}, AM1_{hd}, PM3_{aq} and PM3_{hd}, respectively, which have been outlined by Dixon *et al.* [47].

None of the above described approaches touches on the problem of solvation from the point of view of specific solute–solvent interactions and structure of solvates. The simplest way of achieving this is to perform a Monte Carlo or molecular dynamics calculations on a solute 'immersed' in a box containing a large (but finite) number of solvent molecules [48, 49]. Such an approach, however, requires knowledge of empirical energy functions describing solute–solvent and solvent–solvent interactions.

Information on programs

The application of theoretical methods is nowdays possible due to the wide variety of computer programs available. Semi-empirical and ab initio calculations for small systems can be carried out on personal computers. Advanced calculations and/or those for relatively large molecules require workstations or supercomputers.

To have some idea of the available computer programs we have provided brief information concerning some of them. Numerous quantum chemistry and other programs are distributed by Quantum Chemistry Program Exchange (QCPE) (Indiana University, Bloomington, Indiana 47 405, USA). Very good quantum chemistry programs with statistical thermodynamics and numerous other routines included are: GAUSSIAN (the newest version GAUSSIAN 92/DFT) [50], SPARTAN (the newest version SPARTAN 3.1) [46], GAMESS [51], and MOPAC 93 [52]. GAUSSIAN 92/DFT and MOPAC 93 have included options for the SCRF method [41, 42], while SPARTAN 3.1 – for the Cramer-Truhlar [44, 45] and Dixon *et al.* [47] methods. The most general program for the crystal lattice energy calculations is PCK 83 [53] and one developed by Prof. W. R. Busing (Oak Ridge National Laboratory, Oak Ridge, Tennessee 37 830, USA).

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Zusammenfassung — Eine kurze Übersicht über die theoretischen Möglichkeiten der Bestimmung von energetischen und thermodynamischen Eigenschaften von chemischen Substanzen in gasförmigen und kondensierten (festen und flüssigen) Phasen wird gegeben. Die Überlegungen umfassen quantenchemische Methoden, die die Auswertung von energetischen Größen und statistischen thermodynamischen Abhängigkeiten ermöglichen, die für die Bestimmung anderer thermodynamischer Charakteristika erforderlich sind. Mögliche Anwendungen dieser Methoden werden ebenfalls diskutiert.