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Potential-hypersurface local minima and temperature*

Zdeněk Slanina**
Max-Planck-Institut für Chemie (Otto-Hahn-Institut), W-6500 Mainz, Federal Republic of Germany

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Summary. The presence of several local energy minima on a potential hypersurface is treated in terms of geometry, energy, and harmonic vibrations. Partition functions of the minima are employed in order to treat temperature excitations of rotational-vibrational motions. Proportions of relative stabilities of the individual structures change with temperature (including interchanges of the relative stabilities so that the global energy minimum can even be less populated than a higher local energy minimum). Illustrative examples are given on B_2H_4 and Ga_2H_4 systems. The treatment is suggested as a standard complement of the local-minimum hypersurface representation (before whole potential hypersurfaces are constructed and employed in molecular dynamics treatments).

Key words: Stationary points of potential hypersurfaces – Multiple energy minima – Isomeric interplay at finite temperatures – Global vs. local energy minima – Theory/experiment comparisons

1. Introduction

Potential energy hypersurfaces [1–3] represent [4] a key chemical concept [5, 6]. They can be employed at two different levels: (i) as whole, within molecular dynamics treatments, or (ii) represented by their sole (isolated) stationary (critical) points [7–9], especially local minima. This article deals exclusively with the latter representation (ii). The local-minimum energy and structure characteristics are nowadays routinely completed with evaluation of harmonic vibrational frequencies. A systematic investigation of a potential hypersurface often reveals several different local minima (i.e., several isomers), which all can represent the same observed species. The isomeric relative stabilities can be considerably sensitive to temperature. The computed parameters in fact allow a routine treatment of the temperature effects by means of partition functions in the

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* Dedicated to Prof. Klaus Ruedenberg on the occasion of his 70th birthday

** *Permanent address*: The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, CS-18223 Prague 8-Kobylisy, Czechoslovakia approximation [10] of rigid rotator and harmonic oscillator (RRHO), and this paper gives an illustration.

2. Relative stabilities in an isomeric set

Let us consider a set of n isomers, i.e., a set of local minima of a potential hypersurface(s), under conditions of inter-isomeric thermodynamic equilibrium. We do not impose a stronger condition of some more complex thermodynamic equilibrium (i.e., with respect to dissociation products, etc.). The inter-isomeric equilibrium can be characterized by the mole fractions w_i of the individual isomers. If we deal with ideal-gas conditions, the mole fractions do not depend on the total pressure but on temperature only. The system energetics is described by the potential energy differences ΔE_i related to the global minimum. Addition of the zero-point vibrational energies leads to the ground-state energy differences $\Delta H^o_{0,i}$ (in thermochemical terms – the standard enthalpy changes at the absolute zero temperature [11]).

Geometrical parameters of the local minima and their vibrational frequencies allow construction of the RRHO partition functions q_i of the individual isomers. The isomeric mole fractions are given in the terms as follows [12–14]:

$$w_i = \frac{q_i \exp[-\Delta H^o_{0,i}/(RT)]}{\sum_{j=1}^{n} q_j \exp[-\Delta H^o_{0,j}/(RT)]}, \tag{1}$$

where R denotes the gas constant and T temperature. The application of the RRHO approximation of partition functions should not necessarily have substantial consequences, as a cancellation operates [12] in the right side of Eq. (1). (Interestingly enough, some corrections to the RRHO approximation could be evaluated by means of the correlations suggested by Calder and Ruedenberg [15].)

There is a simplified possibility of reflecting temperature effects on local-minimum relative stabilities, *viz.* by means of so-called simple Boltzmann, configurational or steric factors [16–18], based on the sole potential energy differences ΔE_i. However, these Boltzmann factors do not admit an interchange in the isomeric-stability order with changing temperature.

In the thermodynamical approach [2, 19] to equilibrium isomeric mixtures one can consider either the individual isomers or a pseudospecies – their equilibrium mixture. It creates two classes [2, 19] of quantities – partial and overall. For example, for a reaction we can distinguish standard partial terms ΔX^o_i belonging to the realizations of the reaction with the individual isomers, and the standard overall terms ΔX^o_T belonging to the reaction with the isomeric pseudospecies. The partial and overall terms contain, however, some common terms and it is convenient to eliminate them applying so-called isomerism contributions [19] to thermodynamic terms δX_1:

$$\delta X_1 = \Delta X^o_T - \Delta X^o_1. \tag{2}$$

The δX_1 values generally depend on the choice of the reference isomer labelled by $i = 1$. The most stable species (in low temperature limit) is mostly chosen as the reference structure. Here, X denotes enthalpy ($X = H$), entropy ($X = S$), or heat capacity at constant pressure ($X = C_p$); however, the treatment can, in principle, be considered for any structure-dependent quantity. Two heat-capacity terms can be considered [19]: in addition to the full (relaxation) $\delta C_{p,1}$ term (reflecting the effects of changes in composition upon a temperature change) also isofractional contribution $\delta C_{p,w,1}$ (if w_i are treated as temperature independent).

3. Illustrative examples

Lammertsma and Leszczyński [20] located eight stationary points on the Ga_2H_4 hypersurface (the highest energy approximation applied was the second order MP2 perturbation approach with a valence triply ζ basis set with d-polarization functions). However, the geometry optimization and vibrational analysis were carried out only at HF/3-21G* level. The analysis proved only six of the eight stationary points as local energy minima. For simplicity, the original numbering [20] of the structures is used in this report, too (symmetry followed by the structure number [20] in parentheses): C_{3v} (1), C_{2v} (2), C_{3v} (3), D_{2d} (4), C_{3v} (6), and C_s (7). Figure 1 presents temperature dependencies of the RRHO mole fractions w_i in a broad temperature interval. Crossings of the curves (i.e., relative-stability interchanges) represent a striking feature of Fig. 1. It demonstrates that global energy minimum is not necessarily the most stable species throughout. A higher local minimum can become the most populated isomer at some temperatures instead.

Curtiss and Pople [21] found two local energy minima in B_2H_4 system – doubly-bridged C_{2v} species (lower in energy) and staggered D_{2d} isomer. The structural parameters were evaluated at the MP2/6-31G* level, considering all electrons for calculated correlation energies, and energetics in the geometries was evaluated at the MP4/6-311G** level modified by a number of subsequent corrections. The harmonic vibrational frequencies were evaluated within the HF/6-31G* approach and their scaling by a factor of 0.893 was suggested. Figure 2 presents the temperature behavior. The full w_i factors are compared with the simple Boltzmann terms and a poor applicability of the latter quantities is found. Again, a relative stability interchange is present – the C_{2v} isomer is more populated at the lowest temperatures, with increasing temperature the relative stabilities of both structures become closer and finally they cross. The isomerism contribution to heat capacity in the B_2H_4 system exhibits two maxima

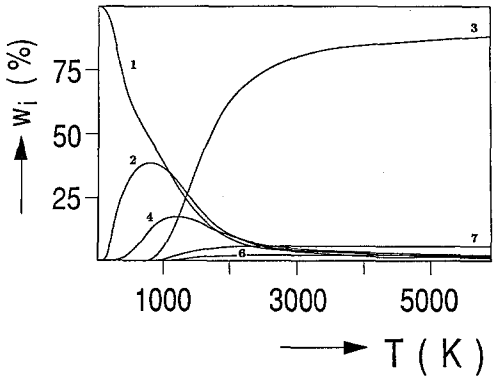

Fig. 1. Temperature dependencies of the weight factors w_i of Ga_2H_4 isomers; the isomers are labelled with numbers introduced in [20]

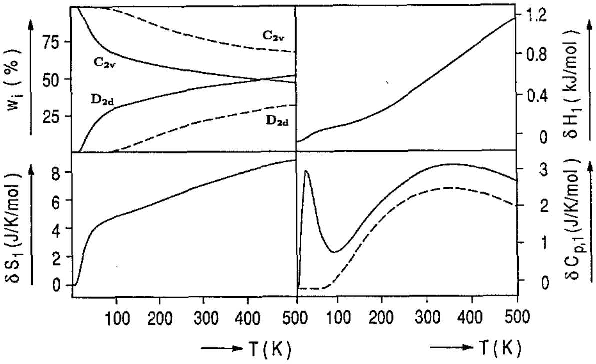

Fig 2. Temperature evolution of B_2H_4 two-membered (C_{2v}, D_{2d}) isomeric system [21]. *Upper left*: Temperature dependencies of the simple Boltzmann factors (*dashed curves*) and the weights w_i. The three other parts: Temperature dependencies of the isomerism contribution (related to the C_{2v} species) to enthalpy δH_1, entropy δS_1, and heat capacity at constant pressure $\delta C_{p,1}$ (relaxation term) or $\delta C_{p,w,1}$ (isofractional term, *dashed line*)

of about the same height (however, upon transfer from the isomerism contribution to the overall heat capacity at constant pressure C_p^o the extremum behavior is conserved only for the lower-temperature maximum).

4. Concluding remarks

There is an inconsistency in our approach. On one hand, the isomer separating barriers should be high enough to allow independency of the motions in the local minima, on the other hand the same barriers should be sufficiently low to allow for establishing the interisomeric equilibrium. The treatment is entirely based on the equilibrium condition and thus, its application can be only formal in some cases. However, a simultaneous rigorous treatment of thermodynamic and kinetic aspects would require knowledge of the whole potential hypersurface. Moreover, in a real situation reaction mixture can contain several other components in addition to the pure isomers. Although ratios of our w_i factors would be transferable, the isomeric effects could be overlapped by contributions from the other members of the mixture.

There are several steps to be carried out within the stationary-point hypersurface representation itself. The kinetic factors can be evaluated within the activated-complex theory, i.e., without leaving the stationary-point hypersurface representation. An inclusion of anharmonicity contributions represents another desirable point. In particular, internal rotation could be treated as a rotational motion rather than a simple harmonic torsion [22] (incidentally, Truhlar [23] recently developed a versatile approximation). These improvements represent first steps towards the limiting situation of fluxional behavior [24–26]. Finally, applications of the treatment in environments other than gas phase should also be studied.

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