CONSEQUENCES OF ISOMERISM OF n-PARTICLES CLUSTERS FOR CONFRONTATION OF THEIR QUANTUM-CHEMICAL CHARACTERISTICS WITH OBSERVABLE QUANTITIES*

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The paper presents a recursion formula between the n-th virial coefficient of a gaseous substance and equilibrium constants of formation of individual isomers of two- to n-particles clusters from the respective molecules. It has been shown how to process both the enthalpy term and equilibrium constant of formation of the individual isomers of two- to n-particles clusters obtained by quantum-chemical calculations. Thus it is possible to confront these partial theoretic characteristics with the macroscopic experimental quantities derived from non-ideal behaviour of substances. The general results are illustrated by quantum-chemical data for water dimers and for two- and three-particles clusters of hydrogen molecule. The results of the present work are promising with respect to possible comparisons of available quantum-chemistry outputs with usual macroscopic experimental data in the field of weak intermolecular interactions.

Recent efforts to use quantum-chemistry methods for generation of basis for statistical-thermodynamic description of liquids began with a study of structure of the molecular complexes formed from n identical molecules[1]. Search for minima on the energy hyper-surfaces of these non-rigid clusters represents a relatively adequate task at the present state of numerical quantum chemistry. On the other hand, however, the obtained information cannot be directly used for the purposes of statistical thermodynamics of liquids. The ideal form of information given for such purpose by quantum-chemistry methods — *i.e.* intermolecular n-particles or, at least, pair potential energy in analytic form[2] — represents, for the time being, quite an extraordinary result with respect to the extent of necessary numerical calculations[3]. It is, therefore, impossible to bring the quantum-chemical calculation up to the value of the experimentally available thermodynamic characteristics of liquids, although such a confrontation would be very desirable with respect to the necessary testing of various methodical approaches in the field of weak intermolecular interactions. An isolated piece of information about the depth and geometry parameters of the potential minimum on extremely flat energy hypersurface of an n-molecular cluster can be confronted with experimental data, of course, only with difficulties. For such confrontation most frequently used are the depth of empirical potentials obtained by fitting to various experimental quantities[2] or the enthalpy term of the respective association process obtained at a non-zero temperature from a spectroscopic experiment (the datum which is, however, accessible only for two-particles-clusters[4]). Both these experimental sources of information correspond only

roughly to the quantities given by theoretical calculation. The problem of confrontation with experimental data was further complicated by a more recent finding of extensive isomerism of weak molecular complexes both in the study at the level of empirical potential[5,6] and in the more sophisticated *ab initio* calculations[1,7]. For example an extensive *ab initio* SCF study[1] showed that the dimer $(H_2O)_2$ represents a mixture of two forms — open and closed. A still more marked isomerism was encountered[1] with the further homologous clusters up to $(H_2O)_8$. The *ab initio* SCF–CI study[7] suggests four possible structures for $(H_2)_2$ differing in their point symmetry group. The available results seem to indicate[6] that isomerism must be expected generally with any n-particles cluster.

Temperature dependences of the respective n-th virial coefficients[8] turned out to be a promising source of information about thermodynamic characteristics of n-particles clusters, especially so in the cases where the contribution of translation of molecules in the potential field resulting from their mutual interaction can be neglected and substituted by translation of independent particles. In this case the virial coefficients can be identified only with the contribution connected with formation of clusters. In the cases not allowing such a neglect the quantum-chemical study of clusters gives an idea about their contribution to virial coefficients. Correct prediction of the virial coefficients values is, of course, indispensable condition for transition to calculations of properties of liquid systems. The efforts to evaluate the n-th virial coefficients thus appear to be an organic intermediate stage in transition from ideal gas phase to liquid.

The efforts to use the cluster concept for interpretation of properties of real gases are somewhat older[9,10]. In these cases, however, the absence of any source of molecular characteristics of clusters prevented a real utilization of this idea. Connection with the generating quantum--chemical methods seems to give possibility to verify both the proper cluster concept and, at the same time, the quality of statements of individual quantum-chemical methods. A correct solution of the both problems must take into account the phenomenon of isomerism of n-particles clusters, *i.e.* find the relations between enthalpy and entropy terms or between equilibrium constants of formation of the respective isomer of n-particles cluster (which represent immediate output of quantum-chemical calculation) and macroscopic quantities obtained from experiment. Solution of this problem and its illustration by numerical examples are dealt with in the present paper.

General Relationships

Let us consider a compound A forming many-particles clusters in gas phase, the clusters from i molecules A being mixtures of m_i various isomeric structures $A_{i,j}$ $(j = 1, 2, ..., m_i)$. For description of equilibria (1) let us choose the equilibrium constants (2) expressed in terms of pressures of the individual components (the standard state the pure component as the ideal gas at 1 atm pressure).

$$iA \rightleftharpoons A_{i,j} \quad (i = 1, 2, ...; \ j = 1, 2, ..., m_i). \tag{1}$$
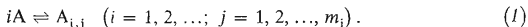
$$K_{i,j} = p_{A_{i,j}}/p_A^i \tag{2}$$

The equilibrium constant (2) is introduced formally also for $i = 1$ assuming that A itself has no isomeric forms, *i.e.* $m_1 = 1$; $K_{1,1} = 1$. The total pressure p of the gase-

ous mixture of compound A and its many-particles clusters is given in Eq. (3) in terms of the equilibrium constants $K_{i,j}$.

$$p = \sum_{i=1}^{\infty} \sum_{j=1}^{m_i} K_{i,j} p_A^i . \tag{3}$$

Let the state behaviour of one mol of compound A be described by an infinite series in terms of the i-th virial coefficients B_i

$$pv = RT \sum_{i=1}^{\infty} B_i v^{(1-i)} . \tag{4}$$

Let ideal behaviour be presumed for all cluster components of the gaseous mixture; this presumption will be discussed below. Hence the fact $B_i \neq 0 \ (i > 1)$ is caused only by the presence of many-particles clusters in the gaseous mixture. Formation of clusters results in decrease of number of mol of the starting compound A, its equation of state assuming the form

$$p_A v = RT - v \sum_{i=2}^{\infty} \sum_{j=1}^{m_i} i K_{i,j} p_A^i . \tag{5}$$

Eq (5) allows to eliminate the variable v from the virial expansion (4) and obtain an alternative expression for the total pressure p

$$p = \sum_{k=1}^{\infty} (RT)^{1-k} B_k \{ \sum_{i=1}^{\infty} \sum_{j=1}^{m_i} i K_{i,j} p_A^i \}^k . \tag{6}$$

Whereas in Eq. (3) p is expressed in terms of $K_{i,j}$ only, in Eq. (6) the coefficients with the powers of the variable p_A are functions of B_k, too. Using the relation for power of infinite series[11] and comparing the expansion coefficients at equal powers of p_A we get a recursion formula for the n-th virial coefficient

$$B_n = (RT)^{n-1} \sum_{j=1}^{m_n} K_{n,j} - \sum_{i=1}^{n-1} c_{i,n-i} B_{n-i} (RT)^i \quad (n > 1) \tag{7}$$

$$c_{i,k} = \frac{1}{i} \sum_{l=1}^{i} (lk - i + l)(l + 1) c_{i-1,k} \sum_{j=1}^{m_{l+1}} K_{l+1,j} \quad (i > 1)$$

$$B_1 = c_{0,k} = 1 .$$

Formulae (7) make it possible to express any virial coefficient as a function of equilibrium constants of cluster formation. For example for the 4th virial coefficient

we get

$$B_4 = (RT)^3 \left(-20 \left(\sum_{j=1}^{m_2} K_{2,j} \right)^3 + 18 \sum_{j=1}^{m_2} K_{2,j} \sum_{j=1}^{m_3} K_{3,j} - 3 \sum_{j=1}^{m_4} K_{4,j} \right). \qquad (8)$$

If the phenomenon of isomerism is excluded, *i.e.* if $m_2 = m_3 = m_4 = 1$, then the formula (8) is reduced to a simpler relation which agrees with the results obtained by Woolley[9] *via* a formally different procedure.

The recursion formula (7) gives an instruction how to traverse from the characteristics of the individual cluster isomers through the equilibrium constants of their formation to the experimentally accessible virial coefficients.

The recursion formula (7) can also be used for solution of the inverse problem *viz* for determination of equilibrium constants of formation of n-particles clusters from the virial coefficients. With the use of formula (7) it is possible to express easily the sums over all isomeric clusters of a given number of molecules $\sum_{j=1}^{m_n} K_{n,j}$ as functions of the second to the n-th virial coefficients. It is, however, impossible to obtain the equilibrium constants of formation of the individual isomers by analysis of virial coefficients. Neither it is possible to differentiate the contributions of the individual isomers when using the second law treatment for determination of the respective standard enthalpy and entropy changes accompanying the cluster formation. From ref.[12] it follows that construction of the van't Hoff's reaction isobar for the summary equilibrium constant of a process involving isomerism of a reaction component leads only to a certain effective value of reaction enthalpy, ΔH_n^0,

$$\Delta H_n^0 = RT^2 \frac{\mathrm{d} \ln \sum\limits_{j=1}^{m_n} K_{n,j}}{\mathrm{d} T}, \qquad (9)$$

which represents the following weighted mean of partial enthalpies $\Delta H_{n,j}^0$ belonging to formation of the j-th isomer of the n-particles cluster

$$\Delta H_n^0 = \sum_{i=1}^{m_n} \frac{K_{n,i}}{\sum\limits_{j=1}^{m_n} K_{n,j}} \Delta H_{n,i}^0. \qquad (10)$$

Analogous situation is encountered with the entropy term, too, where the second law treatment gives only an effective entropy values ΔS_n^0 of formation of the n-particles cluster, any further differentiation between partial entropies $\Delta S_{n,j}^0$ (belonging to individual isomers of the n-particles cluster) being impossssible again[12].

From the recursion formulae (7) it is possible to derive easily the relations between effective value of the enthalpy term ΔH_n^0 and values of the second to n-th virial coefficients; *e.g.* for $n = 4$ the following relation is obtained

$$\Delta H_4^0 = \frac{RT^2}{-16B_2^3/3 + 3B_2B_3 - B_4/3} \left(-16B_2^2 \, dB_2/dT + 3B_3 \, dB_2/dT + \right.$$

$$\left. + 3B_2 \, dB_3/dT - \tfrac{1}{3} \, dB_4/dT\right) - 3RT. \qquad (11)$$

For evaluation of the effective enthalpy term connected with formation of n-particles clusters it is necessary to know the temperature course of the second to the n-th virial coefficients.

Illustrative Examples and Discussion

The relations (7) and (10) give instruction as to how to process the characteristics of individual isomers of n-particles clusters so that a confrontation might be possible with the data obtained from experimental investigation of non-ideality of gas phase. The relations have been derived with the presumption of ideal behaviour of all cluster components of the system investigated. This presumption is forced by the present state of numerical quantum chemistry which can supply data for calculation of thermodynamic characteristics of equilibria (1), but does not allow to calculate interaction potential with a reasonable consumption of computer time. Mastering of calculation of intermolecular potential energy in analytic form would make it possible to interpret the non-ideal behaviour of gas phase as a resultant of the both effects *i.e.* formation of n-particles clusters and translation of all particles in the potential field formed by their mutual interaction.

For evaluation of the second effect the processing of which is well known from statistical thermodynamics at both the classical[13] and quantum-mechanical[14] levels there are, at present, no better bases than empirical potential functions. The relations derived in the previous paragraph will be quite accurate if the quantities B_n involved contain only the contribution due to cluster formation, *i.e.* if the component due to the second effect is excluded from the overall value of the virial coefficients, or if it is negligible[8]. However, since only summary values of the virial coefficients are generally available, their use will give mere estimates of thermodynamic characteristics of cluster formation. There are classes of compounds[15] for which the cluster formation makes fundamental or decisive contribution to the values of virial coefficients. For such compounds our relations will be useful. Their applicability can reasonably be expected to depend on temperature, being better at lower temperatures where there is the highest cluster concentration.

The fact that analysis of experimental data gives only summary values of thermo-

dynamic characteristics of cluster formation, the contributions of partial processes being indistinguishable, indicates a certain formality in the concept of isomerism of non-rigid clusters. This formality is also obvious when considering the rotation--vibration motion of clusters. Not only the independence of rotation and vibration motions within one cluster can be considered (in contrast to rigid molecules), but, in addition to it, the individual forms of clusters will be easily interconverted. Hence neither the rotation-vibration motions of the individual isomers of a cluster will be mutually independent. These circumstances naturally stress the significance of the rotation-vibration partition function of clusters which is necessary for evaluation of thermodynamic characteristics. A sufficiently rigorous description of the rotation--vibration motion and construction of the corresponding partition function will be possible, however, first after the whole energy hypersurfaces of clusters are available from quantum-chemical calculations. The phenomenon of cluster isomerism must be taken into account also in evaluation of infrared spectra of van der Waals molecules. Their analysis is uncertain in giving information about the cluster structure[16], because the potential hypersurfaces are extremely flat, the second reason being probably the overlap of partial spectra of the individual isomers in the summary recorded spectrum.

The relation (10) gives an important information for the search for the minima on the cluster hypersurfaces. At present many quantum-chemical studies try to find the deepest minimum of a potential hypersurface. However, from Eq. (10) it can be seen that contribution of this isomer to the overall value of enthalpy term can be negligible, if a compensation by partial entropy term occurs in unsuitable direction. The more important thing is, therefore, to find all the isomers of the given cluster and evaluate the respective weight factors (10). This evaluation necessitates, of course, the knowledge of the cluster characteristics which may not always be available. Therefore, it seems useful to find, at least, assessments of these factors in some simple cases.

If approximate equality holds for isomers of n-particles cluster

$$\Delta H_{n,1}^0 \approx \Delta H_{n,2}^0 \approx \ldots \approx \Delta H_{n,m_n}^0 \,, \qquad (12)$$

then the enthalpy term of Eq. (10) can be identified with any of the partial enthalpies (12). In cases of comparable thermodynamic stability of all isomers of the n-particles cluster

$$K_{n,1} \approx K_{n,2} \approx \ldots \approx K_{n,m_n} \,, \qquad (13)$$

the weighing according to Eq. (10) can be replaced by simple arithmetic mean. In special cases for the purpose of rough assessment the calculation of the thermodynamic weighted factors (10) can be replaced by mere geometrical consideration[17].

Sometimes also the knowledge of limits, within which the value of summary enthalpy term varies, may be useful. According to ref.[12]

$$\Delta H^0_{n,\,min} \le \Delta H^0_n \le \Delta H^0_{n,\,max}\,, \tag{14}$$

where the indexes min and max mean the minimum and the maximum, respectively, in the set of partial enthalpies $\Delta H^0_{n,i}$. Relation (14) presents a simple test of quantum-chemical results: the summary enthalpy term derived from experimental data should lie within the interval (14).

Water dimer is one of the most frequently studied n-particles clusters. Clementi and coworkers[1] showed the existence of two isomeric forms of this dimer (open and closed having the point symmetry groups C_s and S_2, respectively), using the calculations in the Hartree–Fock approximation and an assessment of the correlation energy. The geometry found by them for the both isomers as well as their zero-point enthalpies were used for approximation of the rotation and vibration partition according to treatment[18], evaluation of the equilibrium constants of formation of the individual isomeric forms of the dimer, and determination of their contribution to the values of the second virial coefficient of water vapour (Table I). The results show that the

TABLE I

Contributions of Isomers of Water Dimer to the Second Virial Coefficient of Water Vapour B_2 $(cm^3\,mol^{-1})$

	Theoretical			
T, K	open form of the water dimer[b]	closed form of the water dimer[c]	both isomers	Experimental[a]
323·16	−349·4	−69·6	−419·1	−838·3
373·16	−130·9	−32·2	−163·1	−451·0
423·16	−62·2	−18·0	−80·2	−283·5
473·16	−34·8	−11·4	−46·3	−196·7
523·16	−21·9	−8·0	−29·9	−145·3
573·16	−15·1	−6·0	−21·1	−112·0
623·16	−11·1	−4·7	−15·8	−89·1
673·16	−8·6	−3·9	−12·5	−72·6
723·16	−6·9	−3·3	−10·2	−59·9

[a] Taken from ref.[19]; [b] $\Delta H^0_{0,2} = -17\cdot196$ kJ mol^{-1}; [c] $\Delta H^0_{0,2} = -12\cdot970$ kJ mol^{-1}.

dimer formation accounts for about 50 per cent of B_2 value at lower temperatures. It must be, however, noted that critical value in this calculation is that of zero-point enthalpy. Especially the magnitude of contribution of correlation energy will probably be assessed with fundamentally more precision in future[1]. Lowering of the term $\Delta H_{0,2}^0$ for the open form by less than 2·4 kJ/mol causes the contribution of this isomer into B_2 to be (at $T = 323\cdot16$ K) just equal to the experimentally found value of this virial coefficient. Although there is no doubt that the both isomers of water dimer contribute significantly to B_2, precise determination of their contributions will need further efforts in evaluating both the zero-point energy and data for construction of rotation-vibration partition function. First then it will be possible to judge the ratio of contributions of the open and the closed forms.

Table II summarizes the results of analysis of temperature dependences of B_2 and B_3 of hydrogen molecule. The experimental values[19,20] of B_2 and B_3 were interlaced by a six-parameter function of temperature, and the values $\Delta H_{T,2}^0$ and $\Delta H_{T,3}^0$ were evaluated at the lowest temperatures of the experimental temperature range. Recently Kochanski and coworkers[7] showed (on the basis of an *ab initio* SCF-CI study) the possibility of four isomers of $(H_2)_2$ cluster. As, however, the basis is lacking for description of rotation-vibration motion in the individual forms of the dimer, neither weighing according to Eq. *(10)* nor determination of magnitude of contributions of these motions to the zero-point energy are possible. If the summary enthalpy term is considered equal to enthalpy of formation of the deepest minimum[7], and its change within 0 to 14 K is neglected, then confrontation of results in Table II and ref.[7] gives a rough assessment of characteristics of the vibration motion. Contribution of four vibrational degrees of freedom (accompanying the dimer formation) to its zero-point energy is represented by the wave number 13 cm^{-1} per each degree of freedom. Remarkably high is the effective value of interaction enthalpy in the case of trimer $(H_2)_3$. However, so far in literature there are no cor-

TABLE II

Effective Enthalpy Terms $\Delta H_{T,2}^0$, $\Delta H_{T,3}^0$ of Formation of Two- and Three-Particles Clusters of Hydrogen Molecule Determined from Experimental Temperature Dependences of the Second and the Third Virial Coefficients

T, K	$\Delta H_{T,2}^0$, J mol^{-1}	T, K	$\Delta H_{T,3}^0$, J mol^{-1}
14[a]	−281	55·75[c]	−3 716
14[b]	−280	55·75[c]	−3 472

[a] B_2 taken from refs[19,20]; [b] B_2 taken from ref.[19]; [c] B_3 taken from ref.[19].

responding *ab initio* calculations of interaction energies in the hydrogen trimer, which initiated a systematic study[21] of higher clusters of H_2 molecules.

The calculation of the effective $\Delta H^0_{T,2}$ and $\Delta H^0_{T,3}$ values from experimental temperature dependences of B_2 and B_3 is, of course, possible for hundreds of compounds[19]. In this way it would be possible to get an extensive set of data useful for testing of quantum-chemical procedures describing weak intermolecular interactions. Usually virial coefficients of any high degree are not subject to measurements, nevertheless they are accessible from the data of state behaviour. This method for obtaining $\Delta H^0_{T,n}$ ($n > 3$) will need a detailed analysis of accuracy of the data obtained. At the same time it is desirable to pay attention to utilization of quantum-chemical calculations for description of rotation-vibration motion in clusters, so that a fundamental source of uncertainty in confronting theoretical with experimental data might be removed. As the cluster concept will probably be a predominant quantum-chemical model of real gas and liquid phase for a long time, it also seems useful to develop procedures enabling an *a priori* determination of number of isomeric structures of a n-particles cluster. In this respect the utilization of the graph theory seems potentially very promising[22].

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