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Multiple-configuration versus single-configuration thermodynamic quantities for water and some other clusters [α,β]

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Abstract

At present, clusters are most usually theoretically studied as local energy minima on potential hypersurfaces; quite typically a manifold occurrence of such minima on one hypersurface is encountered. The cluster isomerism proved in this theoretical way has substantial consequences for comparisons of theory with experiment as well as for interpretation and prediction purposes. It leads to differentiation between two classes of quantities, namely multiple- and single-configuration characteristics. This approach is significant for any structure-dependent property; nevertheless, it has been developed most extensively for thermodynamic characteristics of cluster formation. These problems are illustrated with water clusters, $(CO_2)_2^-$ and other systems, particular attention being paid to the heat capacity term. More generally, even contributions of clusters of different dimensions can be considered for some quantities. The approach is applied to interpretation of the saturated pressure of steam, and temperature increase of relative cluster populations under the saturation condition is rationalized.

INTRODUCTION

Recently rapid development has taken place in the field of experimental and theoretical studies of gas-phase clusters (for survey, see e.g. refs. 1, 2), the clusters themselves serving as possible models for environmental effects and phenomena. These clusters exhibit quite considerable non-rigidity, and often it is difficult to prepare them in suitable concentrations; nevertheless, their partial or even complete structure has been established on the basis of

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observation in a number of cases. A special structural feature of these complexes is the presence of isomerism, which recently has also been proved for some systems by observation. Very recent examples include the isomeric dimers $N_2O \cdot HF$ and $ON_2 \cdot HF$ [3] or $OC \cdot HF$ and $CO \cdot HF$ [4]. A far greater number of pieces of evidence about the isomerism of clusters is however provided by theoretical studies (for survey, see e.g. ref. 5) which established de facto isomerism as a typical (and often even very ample) feature of these species. This isomerism is important not only for considerations of the stability order of individual structures. The possibilities of relatively easy transitions between individual isomers, the nearness of their relative stabilities at some temperatures and rapid changes of relative stability proportions in other temperature intervals, the difficulty of distinguishing between the individual structures experimentally, all lead to the necessity of transition from the structure lying lowest in the potential energy term to consideration of the whole group of isomeric structures and thus of their collective effects. Of course, this whole approach reflects the contemporary state of computational chemistry typically employing, for characterizing potential hypersurfaces, their stationary points. If the whole of these hypersurfaces were available, then the isomerism of clusters would be automatically implicitly involved and treated in the whole hypersurface terms. Finally, an even more general approach can be foreseen, composed of some quantities from contributions of clusters of different dimensions (the clusters possibly also being of isomeric composition).

MULTIPLE ISOMERIC CONFIGURATION TERMS

Let us consider the formation of an isomeric set of clusters $(AB)_i$ $(i = 1, \ldots, n)$ in ideal gas phase

$$A(g) + B(g) = (AB)_i(g) \tag{1}$$

The mutual proportions of these isomeric clusters will be characterized by means of their mole fractions (weight factors) in the equilibrium mixture w_i. Any structure-dependent term corresponding to one individual structure will be called single-configurational, whereas a term corresponding to a whole group of isomers in their equilibrium mixture will be denoted as multiple-configurational. The relation between these two types of quantities can be expressed in terms of mole fractions w_i.

Thusfar, special attention has been paid [6] to the standard thermodynamic characteristics belonging to the processes (1). Thus, for example, the multiple-configurational standard enthalpy change $\Delta H^{\ominus}$ and the respective single-configurational changes $\Delta H_i^{\ominus}$ are related as [7]

$$\Delta H^{\ominus} = \sum_{i=1}^{n} w_i \, \Delta H_i^{\ominus} \tag{2}$$

and similarly for the multiple-configurational and single-configurational entropy changes along the reaction (1)

$$\Delta S^{\ominus} = \sum_{i=1}^{n} w_i \left(\Delta S_i^{\ominus} - R \ln w_i\right) \tag{3}$$

A particularly interesting situation is encountered with the terms of standard changes in heat capacity at constant pressure, multiple-configurational $\Delta C_p^{\ominus}$ and single-configurational $\Delta C_{p,i}^{\ominus}$. The corresponding relations result as temperature derivatives of relation (2), of course with due respect paid to the fact that each member of the product in the sum is temperature-dependent [7]

$$\Delta C_p^{\ominus} = \sum_{i=1}^{n} w_i \, \Delta C_{p,i}^{\ominus} + \frac{1}{RT^2} \left\{ \sum_{i=1}^{n} w_i \left(\Delta H_i^{\ominus}\right)^2 - \left[\sum_{i=1}^{n} w_i \, \Delta H_i^{\ominus}\right]^2 \right\} \tag{4}$$

The relations (2)–(4) form a basis for proper comparisons of theoretical and observed data in the cases where observation did not allow any differentiation between the individual particular structures and resulted in the values of the thermodynamic terms of multiple-configurational nature.

WEIGHT FACTORS AND THEIR TEMPERATURE INTERCHANGES

The link between a quantum-chemical representation of the potential hypersurface of a cluster system in terms of its stationary points and the single- and multiple-configurational characteristics is facilitated by the notion of the partition functions of individual isomeric clusters q_i. Generally, these partition functions can be constructed in various approximations; nevertheless, it is natural to work with the approximation [8] of rigid rotator and harmonic oscillator (RRHO), since just this extent of information is reached by the conventional quantum-chemical characterization of stationary points of hypersurfaces. The weight factors w_i can easily be expressed in terms of these partition functions [7]

$$w_i = \frac{q_i \exp\left(-\Delta H_{0,i}^{\ominus}/RT\right)}{\sum_{j=1}^{n} q_j \exp\left(-\Delta H_{0,j}^{\ominus}/RT\right)} \tag{5}$$

where $\Delta H_{0,i}^{\ominus}$ means the change in ground-state energy along reaction (1), i.e. the change in standard enthalpy at absolute zero.

At the lowest temperatures the highest value is assumed by the weight factor corresponding to the lowest $\Delta H_{0,\mathrm{i}}^{\ominus}$ term, but with increasing temperature the significance of the exponential factors in relation (5) decreases. Thereby a possibility is given for mutual approach of the w_i values, and in principle a relative stability interchange of a pair of isomers of the set studied can occur at a certain temperature T_i. The easiest way is to follow these problems in a two-isomer system, where eqn. (5) is reduced to the simple form

$$w_1 = \frac{q_1}{q_1 + q_2 \exp\left[-\left(\Delta H_{0,2}^{\ominus} - \Delta H_{0,1}^{\ominus}\right)/RT\right]} \tag{6}$$

The quantum-chemical procedure often brings the following situation. Two-fold isomerism is found in a cluster system which is described, as far as the structural and harmonic vibrational characteristics are concerned, in a certain approximation of energy. (For the sake of simplicity we shall suppose that both these isomers are non-linear structures.) Then, the quantum-chemical treatment turns to another, more sophisticated, approximation of energy, but the calculation of potential energy change adopts the structure found in the previous approximation. This leads to two sets of cluster parameters for calculation of the weight factors w_1 and w_2. These sets have identical structural and vibrational data; they differ only in the energy terms.

Let there exist, within the first set of parameters, a temperature $T_{i,1}$ at which equimolarity of both structures is reached. If we now turn to the second set of parameters, a real change is only observed with the term $\Delta H_1 = \Delta H_{0,2}^{\ominus} - \Delta H_{0,1}^{\ominus}$ which now assumes the value ΔH_2. A natural, practical task consists of evaluating the $T_{i,2}$ value (from the $T_{i,1}$, ΔH_1, and ΔH_2 terms) at which equimolarity is reached in the second of both approximations of potential energy. If besides the RRHO approximation still another simplification is used (namely substitution of the usual vibrational partition function by its high-temperature limit, i.e., by the expression [9] $kT/h\omega$, where ω denotes the corresponding harmonic vibrational frequency), then it can be shown that

$$T_{i,2} = T_{i,1}\, \Delta H_2/\Delta H_1 \tag{7}$$

The application of this high-temperature limit is justified because the critical intermolecular frequencies in the clusters are usually very low; hence the governing term T/ω assumes sufficiently high values relatively soon.

THE $(CO_2)_2^-$(g) ISOMERIC SYSTEM

An interesting isomeric cluster system was described recently in an ab initio study in flexible basis set (6-31 + G*) [10] with involvement of electron correlation by means of second-order (MP2) and third-order (MP3) Møller–Plesset perturbation theory, viz., two isomers of the anionic cluster $(CO_2)_2^-$(g) having the point groups of symmetry D_{2d} and C_s. In these two approaches, however, only the potential energy term was determined, whereas the structure and vibration frequencies resulted from the Hartree–Fock treatment in the 6-31G basis set. The separation of the two structures in terms of potential energy is 30 and 20 kJ mol^{-1} in the MP2 and MP3

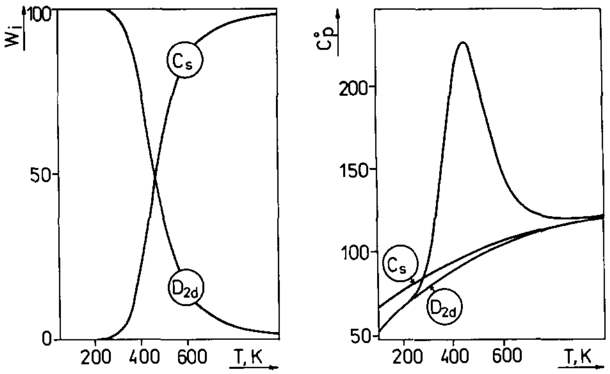

Fig. 1. Left: temperature dependence of the weight factors w_i of the D_{2d} and C_s isomers of $(CO_2)_2^-$(g) in the MP2 approach (w_i in %). Right: one- and two-component terms of heat capacity at constant pressure for the isomeric system (J K^{-1} mol^{-1}).

approximations, respectively, the D_{2d} structure being more stable in this scale.

Figure 1 presents the temperature dependence of this isomeric interplay for the MP2 approach to the potential energy term. It can be seen that increasing temperature results in a quite fast mutual approach of the relative stabilities of both structures. Their equimolarity is reached at about 469.1 K, whereafter the relative stabilities are of course interchanged.

The right-hand side of Fig. 1 shows that this relative stability interchange has its distinct consequences at the level of the term of two-component standard heat capacity at constant pressure, C_p^0, which differs markedly from the partial terms corresponding to the individual components. In this case not only a distinct quantitative enhancement but also a substantial qualitative difference is encountered, viz., the presence of a rather sharp temperature maximum.

The $(CO_2)_2^-$(g) system does not represent a solitary example of an isomeric cluster system with substantial isomerism effects. Table 1 presents an illustrative survey of the formation of four neutral cluster dimers with twofold isomerism [11–14] and of the system from Fig. 1. Although the effects of isomerism are greatest in the last system mentioned, it is nevertheless obvious that this phenomenon is significant in all the systems considered.

Table 2 presents an application of the approximate evaluation formula (7) to the case of the $(CO_2)_2^-$(g) system in the transition from MP2 to MP3 energetics and vice versa. It can be stated that this evaluation formula can serve for reasonable assessments of the stability inversion temperatures with the change of energy term. It is interesting that for every value of the ΔH_2 term (under the presumption of equal parity of the terms ΔH_1 and ΔH_2, i.e. $\Delta H_1 \, \Delta H_2 > 0$) this treatment guarantees the existence of the inversion temperature $T_{i,2}$ (although, of course, it will be unreasonably high from

TABLE 1

Illustrative examples of relatively large differences between the partial $\Delta C_{p,i}^{\ominus}$ and overall $\Delta C_p^{\ominus}$ standard [a] changes of heat capacity at constant pressure

Process	T (K)	$\Delta C_{p,1}^{\ominus}$	$\Delta C_{p,2}^{\ominus}$	$\Delta C_p^{\ominus}$
$2CO_2(g) = (CO_2)_2(g)$ [b]	140	6.95	7.68	22.1
$HF(g) + ClF(g) = HF\text{–}ClF(g)$ [c]	50	-14.9	-16.0	2.03
$CO(g) + HF(g) = CO\text{–}HF(g)$ [d]	230	3.81	5.54	15.6
$HF(g) + Cl_2(g) = HF\text{–}Cl_2(g)$ [e]	60	0.004	-3.30	14.2
$2CO_2(g) + e^-(g) = (CO_2)_2^-(g)$ [f]	400	-14.2	-10.2	98.4
				33.7

[a] Ideal gas state (standard state is irrelevant); in J K^{-1} mol^{-1}.

[b] 1, parallel dimer; 2, T form [11].

[c] 1, $HF \cdot ClF$; 2, $ClF \cdot HF$ [12].

[d] 1, $OC \cdot HF$; 2, $CO \cdot HF$ [13].

[e] 1, $Cl_2 \cdot FH$; 2, $Cl_2 \cdot HF$ [14].

[f] 1, D_{2d}; 2, C_s [10]; the two-component term in the upper and lower line corresponds to the MP2 and MP3 approximation, respectively.

TABLE 2

Exact and estimated temperature position of the equimolarity points [a] $T_{i,1}$ and $T_{i,2}$ in the $(CO_2)_2^-(g)$ isomeric system within the MP2 and MP3 approaches to energetics

Term	Temperature (K)	
	Exact	Estimated
$T_{i,1}$	469.1	504.3
$T_{i,2}$	317.9	295.7

[a] $T_{i,1}$ and $T_{i,2}$ denote relative stability interchange temperatures in the MP2 and MP3 approaches, respectively.

observational point of view for some ΔH_2 values). It remains an open question as to whether or not this existence theorem would also be valid after transition from the high-temperature limit to the conventional vibrational partition function.

WATER–DIMER AUTOISOMERIZATIONS

So far we have considered an association equilibrium and the standard thermodynamic terms corresponding thereto. However, a deeper analysis shows [15,16] that the above formulae can also be applied quite strightforwardly to rate processes, providing parallel isomerism was proved in their activated complexes. It is, for example, the case of the water–dimer autoisomerization kinetics

$$(H_2O)_2(g) \rightarrow X_i^{\neq} \rightarrow (H_2O)_2(g) \qquad (8)$$

TABLE 3

Temperature dependences [a] (J K $^{-1}$ mol^{-1}) of partial ($\Delta C^{\neq}_{p,i}$) and overall ($\Delta C^{\neq}_{p}$) activation heat capacities for $(H_2O)_2$ interconversion [b]

T (K)	$\Delta C^{\neq}_{p,C_s}$	$\Delta C^{\neq}_{p,S_2}$	$\Delta C^{\neq}_{p,C_{2v}}$	$\Delta C^{\neq}_{p}$
100	−6.80	−7.33	−3.90	−4.36
200	−7.62	−9.64	−5.34	−2.83
298.15	−7.74	−9.63	−6.40	−3.81
300	−7.74	−9.63	−6.42	−3.83
400	−7.91	−9.33	−7.05	−4.99
500	−8.03	−9.09	−7.42	−5.82

[a] Calculated from the MCY-B potential [17,18].

[b] Partial interconversions are connected with the activated complexes of C_s, S_2 or C_{2v} symmetries and the potential barrier height of 0.95, 3.09 or 7.47 kJ mol^{-1}, respectively.

which can proceed through three different parallel activated complexes [16,17], belonging to C_s, S_2 and C_{2v} point groups of symmetry. Per analogiam the partial and overall activation terms can be introduced.

Table 3 presents the interplay between the partial and overall activation heat capacity terms $\Delta C^{\neq}_{p,i}$ and $\Delta C^{\neq}_{p}$, respectively. The terms were evaluated within the MCY-B potential [18] which was recently proved [19] to satisfactorily reproduce observed thermodynamic terms of water-dimer formation. Similar to the finding in equilibrium processes, the activated-complex isomerism produces an extremum course of temperature dependence of the overall term $\Delta C^{\neq}_{p}$ (while the course of the partial terms is monotonous). Such a temperature maximum could serve as experimental evidence for activated-complex isomerism.

It can be concluded that the isomeric interplay (in both equilibrium as well as rate situations) can bring such effects for the differences between multi- and single-component terms that it can undoubtedly become very significant for comparisons of quantum-chemical theory with the observed data as well as for prediction and interpretation purposes.

TOWARDS COMPOSING CONTRIBUTIONS OF CLUSTERS OF DIFFERENT DIMENSIONS

A generalization from isomeric clusters to contributions of clusters of variable dimensions is clearly desirable, though such an approach is now quite rare. An example can be served by the study [20] of the hydration of methanol simulated by cluster cavities of different dimensions.

Another interesting example is given by the RRHO MCY-B/EPEN model of gas-phase water clusters [21,22]. Within the model, clusters of any dimension can be taken into account and, thus, a property of steam can be expressed in terms of the cluster contributions. Particularly, the pressure P

of the cluster mixture can be simply expressed through the cluster partial pressures p_i

$$P = \sum_{i=1}^{\infty} p_i \tag{9}$$

When the model was applied to the pressure of the saturated steam it was found [23] that relative cluster populations (namely dimers and trimers) in the equilibrium mixture increase at the expense of the monomer. This result may seem surprising (though it may be indirectly conjectured from observation [24]) and therefore its rationalization is required.

Let us limit our attention to monomers and dimers.

$$P = p_1 + p_2 \tag{10}$$

In terms of the mole fraction of the monomer x_1 and the equilibrium constant of water-dimer formation K_2, eqn. (10) can be transferred to

$$1 = x_1 + x_1^2 P K_2 \tag{11}$$

Temperature differentiation of eqn. (11) and application of the van't Hoff equation [9] gives

$$\frac{\mathrm{d} \ln K_2}{\mathrm{d}T} = \frac{\Delta H_{T,2}^{\ominus}}{RT^2} \tag{12}$$

where $\Delta H_{T,2}^{\ominus}$ denotes the standard molar enthalpy of water dimerization (a tacit trivial condition $K_2 \neq 0$ is presupposed), together with the Clausius–Clapeyron equation [9]

$$\frac{\mathrm{d} \ln P}{\mathrm{d}T} = \frac{\Delta H_{T,\mathrm{v}}}{RT^2} \tag{13}$$

where $\Delta H_{T,\mathrm{v}}$ denotes the molar heat of vaporization of water [25], yields

$$\frac{\mathrm{d}x_1}{\mathrm{d}T} = -\frac{x_1^2 P K_2}{(1 + 2x_1 P K_2) RT^2} \left(\Delta H_{T,2}^{\ominus} + \Delta H_{T,\mathrm{v}} \right) \tag{14}$$

Values of terms $\Delta H_{T,2}^{\ominus}$ (from the MCY-B evaluation [17–19]) and $\Delta H_{T,\mathrm{v}}$ (from compilation [25]) can readily be compared. Table 4 shows that $|\Delta H_{T,2}^{\ominus}| < \Delta H_{T,\mathrm{v}}$ so that $\Delta H_{T,2}^{\ominus} + \Delta H_{T,\mathrm{v}} > 0$, and consequently

$$\frac{\mathrm{d}x_1}{\mathrm{d}T} < 0 \tag{15}$$

The meaning of relation (15) is clear: in saturated steam (composed of monomers and dimers only) the mole fraction of monomers decreases with increasing temperature. Hence, the mole fraction of dimer increases within the model.

The reasoning indicates that a saturated vapour becomes a more complex cluster mixture at higher temperatures. This represents another impetus to

TABLE 4

Temperature dependences of the standard [a] molar enthalpy change upon gas-phase water dimerization [b] $\Delta H^{\ominus}_{T,2}$ and molar heat of vaporization [c] $\Delta H_{T,\mathrm{v}}$ of water

T (K)	$\Delta H^{\ominus}_{T,2}$ (kJ mol^{-1})	$\Delta H_{T,\mathrm{v}}$ (kJ mol^{-1})
300	−16.0	43.9
373.15	−15.2	40.7
400	−14.9	39.3
500	−13.5	32.9
600	−12.1	21.1

[a] Standard state; an ideal gas at 1 atm = 101 325 Pa pressure.
[b] Calculated from the MCY-B potential [17–19].
[c] Interpolated from data [25].

consider various quantities as a combination of contributions from clusters of different dimensions, in addition the clusters themselves generally being composed of isomers.

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