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Cluster isomerism and its thermodynamic consequences—a feature of growing importance [α,β]

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Abstract

Thermodynamic consequences of cluster isomerism are surveyed, and are illustrated for the HF(g)–ClF(g) association system (containing the species HF·ClF and ClF·HF). The possibility is pointed out of isomeric relative stability interchange, as well as of a pronounced temperature maximum in the heat capacity term. The results can be important for theory–experiment comparisons, and possible consequences are briefly discussed.

Recently, structural and spectroscopic features and energetics of several gas-phase molecular clusters exhibiting isomerism have been investigated. The thermodynamics of some of them have also been evaluated [1–4]; see Table 1. This report deals with the thermodynamic consequences of the cluster isomerism [5], illustrating them by means of the association system [6] HF (g)–ClF(g) (namely, using the SCF data [6] and the rigid-rotor and harmonic-oscillator partition functions [5] with the exception of the torsional motion treated as a free internal rotation). The system was proved [6] to possess two different local energy minima, namely HF · ClF and ClF · HF.

An n-membered isomeric mixture is characterized by the mole fractions w_i of the individual isomers. The populations can be evaluated [5,7,8] using the standard enthalpy terms at the absolute zero temperature $\Delta H_{0,i}^{\ominus}$ and the isomeric partition functions q_i

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

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TABLE 1

Examples of cluster systems with two-fold isomerism and characterization of their equimolarity point $T_{50\%}$ and temperature position T_{max} of the maximum in the isomerism contribution to heat capacity $\delta C_{p,1}$

System	$T_{50\%}$ (K)	T_{max} (K)	$\delta C_{p,1}$ (J K^{-1} mol^{-1})	Ref.
$(CO_2)_2^-$(g) [a]	469	442	134	1
N_2O(g)–H_2O(g) [b]	879	580	19	2
HF(g)–ClF(g) [c]	76	46	17	This work
N_2O(g)–HF(g) [d]	–	118	5.3	3
HF(g)–HCl(g) [e]	–	53	4.9	4

[a] D_{2d} and C_s structures.
[b] $N_2O\cdot HOH$ and $ON_2\cdot HOH$ non-linear structures.
[c] HF·ClF and ClF·HF non-linear structures.
[d] Linear $ON_2\cdot HF$ and bent $N_2O\cdot HF$ structures.
[e] HF·HCl and HCl·HF quasi-linear structures.

where R denotes the gas constant and T temperature. For isomeric systems it has become customary to distinguish two categories of quantities [5]: the standard partial terms $\Delta X_i^\ominus$ belonging to the individual isomers, in our example to the reactions

$$\mathrm{HF(g) + ClF(g) = HF\cdot ClF(g)} \tag{2}$$

$$\mathrm{HF(g) + ClF(g) = ClF\cdot HF(g)} \tag{3}$$

and the standard overall terms $\Delta X_T^\ominus$ belonging to the total process with a pseudospecies represented by the equilibrium isomeric mixture

$$\mathrm{HF(g) + ClF(g) = HF{-}ClF(g)} \tag{4}$$

Finally, so-called isomerism contributions to thermodynamic terms δX_1 were introduced

$$\delta X_1 = \Delta X_T^\ominus - \Delta X_1^\ominus \tag{5}$$

The values of δX_1 generally depend on the choice of the reference isomer labelled by $i = 1$. It is convenient that the most stable species (in the low temperature region) be chosen as the reference structure. In our connection, X denotes a standard thermodynamic term (namely: 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. It holds for $X = C_p$

$$\delta C_{p,1} = \delta C_{p,w,1} + \frac{1}{RT^2}\left[\sum_{i=1}^{n} w_i\left(\Delta H_i^\ominus - \Delta H_1^\ominus\right)^2 - (\delta H_1)^2\right] \tag{6}$$

where $\delta C_{p,w,1}$ stands for the so called isofractional isomerism contribution to heat capacity

$$\delta C_{p,w,1} = \sum_{i=1}^{n} w_i\left(\Delta C_{p,i}^\ominus - \Delta C_{p,1}^\ominus\right) \tag{7}$$

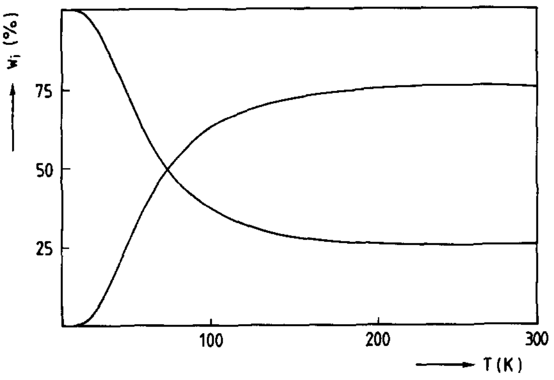

Fig. 1. Temperature dependence of the mole fractions w_i of HF·ClF (the curve lying higher in the low-temperature limit) and ClF·HF structures of the HF(g)–ClF(g) system.

and the isomerism contribution to enthalpy is given by

$$\delta H_1 = \sum_{i=1}^{n} w_i \left(\Delta H_i^{\ominus} - \Delta H_1^{\ominus} \right) \tag{8}$$

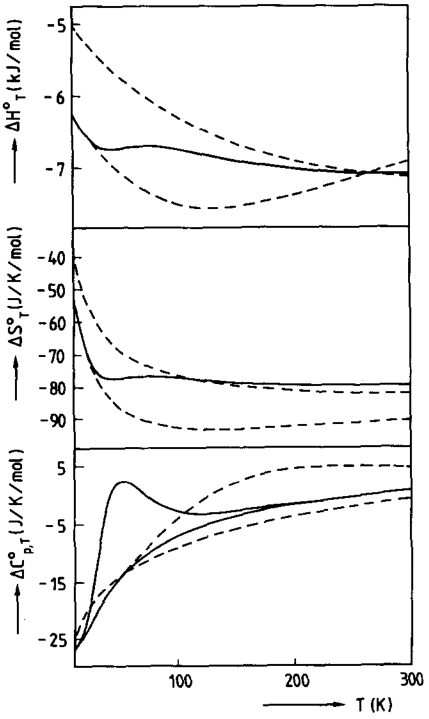

Fig. 2. Temperature dependences of the partial (dashed curves) and overall (solid curve) standard enthalpy $\Delta H_T^{\ominus}$ (top), entropy $\Delta S_T^{\ominus}$ (middle), and heat capacity at constant pressure $\Delta C_{p,T}^{\ominus}$ (bottom) changes for HF(g) and ClF(g) associations; the other solid curve with heat capacity dependence represents the isofractional overall term.

The $\delta C_{p,1}$ term in eqn. (6) applies to the effects of changes in composition upon the corresponding temperature change, and it is therefore called the relaxation isomerism contribution to heat capacity. (In the isofractional contribution $\delta C_{p,w,1}$ derivation, w_i values are considered to be temperature independent.)

The isomerism contributions represent a useful tool for evaluation of the isomeric effects, and also they allow easy generation of the overall terms. In an isomeric system, there can be two interesting events—interchange of relative stabilities and a pronounced maximum in the $\delta C_{p,1}$ term (Table 1). Both events are present in the HF–ClF system (the stability interchange can be well seen in Fig. 1), although the maximum height is rather moderate [compared e.g., with ≈ 134 J K^{-1} mol^{-1} maximum height found [1] for the $(CO_2)_2^-(g)$ isomeric system]. Figure 2 presents temperature dependences of the partial and overall standard changes of enthalpy, entropy, and heat capacity at constant pressure for reactions (2)–(4). From the experimental point of view it is particularly interesting that a maximum exists also in the overall (relaxation) $\Delta C_{p,T}^{\ominus}$ term. Finally, it should be realized that the treatment deals with thermodynamic equilibrium, which is not always present [9–11] under real experimental conditions.

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