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Cl_2–HF(g): THERMODYNAMICS OF THE SYSTEM WITH TWO-FOLD ISOMERISM *

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ABSTRACT

The thermodynamics of the gas-phase complex Cl_2–HF(g) were studied with respect to the recent finding that this complex is represented by two isomeric structures, namely hydrogen-bonded $Cl_2 \cdot HF$ and non-hydrogen-bonded $HF \cdot Cl_2$. In this system the structure which is more stable in terms of the ground-state energy ($HF \cdot Cl_2$) gradually loses its predominance with increasing temperature; equimolar amounts of the two structures in the equilibrium mixture are attained at 97 or 111 K depending on the computational treatment used. This isomerism has distinct consequences for the thermodynamics of the system. Particularly marked effects are observed in the overall heat capacity term; the isomerism contribution reaches its highest value at the temperatures 52 or 59 K depending on the computational treatment used (contributions are 14.3 or 14.2 J K^{-1} mol^{-1} respectively).

INTRODUCTION

Recently, the thermodynamics of several gas-phase molecular complexes which exhibit isomerism have been investigated, e.g. the systems *cis*-$(NO)_2$ and *trans*-$(NO)_2$ [2], CO · HF and OC · HF [3] and the isomeric systems formed by two structural forms $(CO_2)_2$ [4,5] or $(CO_2)_2^-$ [6]. Such isomeric systems often exhibit interchanges in the relative stability of the isomeric structures with changing temperature [1–10]; this also has consequences for the values of the standard thermodynamic functions of such systems. Moreover, molecular complexes can exhibit an unusually large dependence on temperature, and values of temperature derivatives are obtained which are not frequently observed with other types of isomeric systems [11–13]. Increasing interest has been shown recently in the thermodynamic aspects of the formation of a few particle clusters [14–24]; this is directly connected with the rapid development of the investigations of clusters in general [25–27]. This paper deals with isomerism in the system HF–Cl_2(g) [28,29].

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* Part XLV in the series Multimolecular Clusters and Their Isomerism (for part XLIV, see ref. 1).

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CHARACTERIZATION OF THE HF–Cl_2(g) SYSTEM

In a theoretical study [29] two local minima were found on the potential hypersurface of the HF–Cl_2 system. They represent the hydrogen-bonded structure $Cl_2 \cdot HF$ and the non-hydrogen-bonded (i.e. fluorine-bonded) structure $HF \cdot Cl_2$. The structural, vibrational and energy characteristics of both isomers were evaluated [29] within two different computational approximations (denoted as SCF and CPF) differing in the description of electron correlation. Both the isomers are non-linear structures, which implies the presence of four intermolecular vibrational modes; these were evaluated [29] using the harmonic approximation. Two intramolecular frequencies were identified (with their values) in the free monomer units. The structural, vibrational and energy parameters of these monomers were also evaluated in terms of the SCF and CPF approximations.

Table 1 presents the energetics of the two association processes

$$HF(g) + Cl_2(g) = HF \cdot Cl_2(g) \qquad (1)$$

$$HF(g) + Cl_2(g) = Cl_2 \cdot HF(g) \qquad (2)$$

In addition to the term of potential energy change ΔE_i, Table 1 also lists the ground-state energy change which is equivalent to the standard enthalpy change at absolute zero $\Delta H^{\ominus}_{0,i}$ (i denotes either $HF \cdot Cl_2$ or $Cl_2 \cdot HF$ or, possibly, 1 or 2). The non-hydrogen-bonded structure appears to be more stable in both the approximations (SCF and CPF) and on both energy scales (ΔE_i and $\Delta H^{\ominus}_{0,i}$).

TEMPERATURE DEPENDENCE OF THE RELATIVE STABILITY OF THE TWO ISOMERS

If the relative stabilities of the two isomers are to be evaluated at non-zero temperatures, then in addition to the $\Delta H^{\ominus}_{0,i}$ terms, the partition functions must also be involved, thus enabling a description to be given of the

TABLE 1

Potential energy ΔE_i and ground-state energy [a] $\Delta H^{\ominus}_{0,i}$ changes for the formation of $HF \cdot Cl_2$ and $FH \cdot Cl_2$ structures (in kJ mol^{-1})

Process	Type of dimer	SCF [b]		CPF [b]	
		ΔE_i	$\Delta H^{\ominus}_{0,i}$	ΔE_i	$\Delta H^{\ominus}_{0,i}$
$HF(g)+Cl_2(g) = HF \cdot Cl_2(g)$	Non-hydrogen-bonded	−3.18	−1.35	−3.47	−1.62
$HF(g)+Cl_2(g) = Cl_2 \cdot HF(g)$	Hydrogen-bonded	−2.01	0.44	−2.55	−0.06

[a] The standard enthalpy change at absolute zero.

[b] The SCF and CPF treatments are described in ref. 29.

contributions of the rotational–vibrational motions of both isomers (for the purpose of evaluation of relative stability of the isomeric structures it is irrelevant to consider the monomer units). With regard to the amount of information available about the two isomeric structures the consideration must be confined to the RRHO approximation of the partition function [30]. A very convenient means of evaluation of the relative stability of the two isomers in the equilibrium mixture is the proportion of their mole fractions w_i in the mixture [31].

Table 2 shows the temperature dependence of these equilibrium mole fractions from both approximations (SCF and CPF). Of course, at the lowest temperatures the predominant structure is that stable at absolute zero, i.e. the non-hydrogen-bonded isomer; however, as the temperature approaches the limit of approximately 100 K the two isomers become equally stable and equimolar amounts of the isomers are obtained. Equal stabilities are reached at the temperatures of 110.9 and 96.6 K for the approximations SCF and CPF respectively. Furthermore, an increase in temperature causes a gradual increase in the amount of the hydrogen-bonded structure at the expense of the non-hydrogen-bonded structure. The decrease in stability of the latter structure is more rapid in the CPF approximation, although both approximations give the same qualitative picture.

TABLE 2

Temperature dependence of the weight factors [a] w_i of the equilibrium mixture of the $HF \cdot Cl_2(g)$ and $Cl_2 \cdot HF(g)$ structures

T (K)	SCF		CPF	
	w_1 (%)	w_2 (%)	w_1 (%)	w_2 (%)
20	100.0	0.01	99.9	0.06
50	90.5	9.5	84.8	15.2
100	54.7 [b]	45.3 [b]	48.5 [c]	51.5 [c]
150	39.2	60.8	35.8	64.2
200	32.5	67.5	30.4	69.6
250	28.9	71.1	27.5	72.5
298.15	26.7	73.3	25.8	74.2
300	26.7	73.3	25.7	74.3
400	24.2	75.8	23.7	76.3
500	22.8	77.2	22.6	77.4
750	21.0	79.0	21.2	78.8
1000	20.2	79.8	20.6	79.4

[a] Mole fractions; $i = 1$ denotes the non-hydrogen-bonded isomer, $i = 2$ denotes the hydrogen-bonded isomer.

[b] Equimolarity is reached at $T = 110.9$ K.

[c] Equimolarity is reached at $T = 96.6$ K.

ISOMERISM CONTRIBUTIONS TO THERMODYNAMICS: PARTIAL vs. OVERALL TERMS

With regard to the experimental observation of the thermodynamics of reactions (1) and (2), it is clear that rather than differentiating between the two isomeric forms it is possible to follow the system HF–Cl_2(g) as a whole. Thereby we arrive at the overall process

$$\mathrm{HF(g)} + \mathrm{Cl_2(g)} = \mathrm{HF{-}Cl_2(g)} \qquad (3)$$

and at the necessity of differentiating between the overall and partial thermodynamic characteristics [32,33]. The processes (1) and (2) will be characterized by the partial values of standard changes of enthalpy $\Delta H_i^{\ominus}$, entropy $\Delta S_i^{\ominus}$ and heat capacity at constant pressure $\Delta C_{p,i}^{\ominus}$, process (3) will be characterized by the corresponding overall terms $\Delta H_T^{\ominus}$, $\Delta S_T^{\ominus}$ and $\Delta C_{p,T}^{\ominus}$. The relationships between these two types of quantities have been described elsewhere [32,33].

For an easier appreciation of the role of isomerism in thermodynamics it is convenient to consider [32,33] the so-called isomerism contributions $\delta X_1^{\mathrm{iso}}$ to values of thermodynamic functions; these are defined as the difference between the overall values $\Delta X_T^{\ominus}$ and the partial values $\Delta X_1^{\ominus}$ of the isomer which is the most stable in the region of very low temperatures ($X = H$, S or C_p). The values of these isomerism contributions are obviously connected

TABLE 3

Temperature dependences of the isomerism contributions [a] to enthalpy $\delta H_1^{\mathrm{iso}}$, entropy $\delta S_1^{\mathrm{iso}}$ and heat capacity $\delta C_{p,1}^{\mathrm{iso}}$ in the HF–Cl_2 ideal gas-phase equilibrium system

T (K)	SCF			CPF		
	$\delta H_1^{\mathrm{iso}}$ (kJ mol^{-1})	$\delta S_1^{\mathrm{iso}}$ (J K^{-1} mol^{-1})	$\delta C_{p,1}^{\mathrm{iso}}$ (J K^{-1} mol^{-1})	$\delta H_1^{\mathrm{iso}}$ (kJ mol^{-1})	$\delta S_1^{\mathrm{iso}}$ (J K^{-1} mol^{-1})	$\delta C_{p,1}^{\mathrm{iso}}$ (J K^{-1} mol^{-1})
20	0.0003	0.01	0.15	0.0009	0.05	0.44
50	0.169	4.21	12.8 [b]	0.235	6.08	14.3 [c]
100	0.733	12.3	6.50	0.706	13.1	4.13
150	0.914	13.9	1.79	0.806	13.9	0.76
200	0.966	14.2	0.57	0.823	14.0	0.08
250	0.984	14.3	0.20	0.822	14.0	−0.08
298.15	0.990	14.3	0.07	0.817	14.0	−0.11
300	0.990	14.3	0.06	0.817	14.0	−0.11
400	0.991	14.3	−0.01	0.806	14.0	−0.10
500	0.989	14.3	−0.03	0.797	14.0	−0.08
750	0.983	14.3	−0.02	0.783	13.9	−0.04
1000	0.978	14.3	−0.01	0.775	13.9	−0.02

[a] Related to the non-hydrogen-bonded isomer as the reference structure.

[b] Maximum in the $\delta C_{p,1}^{\mathrm{iso}}$ term is reached at 59.2 K with the value of 14.2 J K^{-1} mol^{-1}.

[c] Maximum in the $\delta C_{p,1}^{\mathrm{iso}}$ term is reached at 51.7 K with the value of 14.3 J K^{-1} mol^{-1}.

with the choice of the reference isomer (the choice of the most stable isomer at very low temperatures, i.e. isomer 1, represents a reasonable convention [32,33]). Table 3 presents the temperature dependences of the isomerism contributions to enthalpy, entropy and heat capacity related to the non-hydrogen-bonded structure as the reference structure. Again it can be stated that both the approximations studied [29] lead to the same qualitative picture. The values of the isomerism contributions appear to be significant for all of the three thermodynamic terms considered. In addition, it can be seen that the $T\delta S_1^{\text{iso}}$ term exceeds the corresponding δH_1^{iso} term sometimes by as much as one order of magnitude. The values of all these contributions, especially those at low temperatures, are comparable to or of greater

TABLE 4

Partial and overall standard [a] enthalpies [b] $\Delta H_x^{\ominus}$, entropies [b] $\Delta S_x^{\ominus}$ and heat capacities at constant pressure [b] $\Delta C_{p,x}^{\ominus}$ of HF(g) and Cl_2(g) associations

T (K)	SCF			CPF		
	$\Delta H_x^{\ominus}$ (kJ mol^{-1})	$\Delta S_x^{\ominus}$ (J K^{-1} mol^{-1})	$\Delta C_{p,x}^{\ominus}$ (J K^{-1} mol^{-1})	$\Delta H_x^{\ominus}$ (kJ mol^{-1})	$\Delta S_x^{\ominus}$ (J K^{-1} mol^{-1})	$\Delta C_{p,x}^{\ominus}$ (J K^{-1} mol^{-1})
$HF(g) + Cl_2(g) = HF \cdot Cl_2(g)$						
20	−1.70	−61.0	−16.8	−1.97	−60.0	−16.3
50	−1.95	−69.5	−2.27	−2.22	−68.5	−2.55
100	−1.85	−68.4	4.60	−2.13	−67.5	4.45
200	−1.22	−64.1	7.28	−1.51	−63.3	7.23
298.15	−0.47	−61.1	7.84	−0.76	−60.3	7.82
500	1.15	−57.0	8.14	0.86	−56.1	8.14
1000	5.26	−51.3	8.27	4.97	−50.4	8.27
$HF(g) + Cl_2(g) = Cl_2 \cdot HF(g)$						
20	0.12	−43.1	−15.8	−0.36	−41.4	−16.1
50	−0.17	−52.7	−5.24	−0.67	−51.9	−6.00
100	−0.23	−53.8	1.73	−0.76	−53.3	1.50
200	0.21	−50.9	6.13	−0.32	−50.5	6.07
298.15	0.88	−48.2	7.27	0.34	−47.8	7.24
500	2.43	−44.2	7.93	1.89	−43.8	7.92
1000	6.49	−38.6	8.22	5.94	−38.2	8.21
$HF(g) + Cl_2(g) = HF\text{–}Cl_2(g)$						
20	−1.70	−61.0	−16.6	−1.97	−59.9	−15.9
50	−1.78	−65.3	10.5	−1.98	−62.4	11.7
100	−1.12	−56.1	11.1	−1.42	−54.5	8.59
200	−0.25	−50.0	7.85	−0.68	−49.3	7.31
298.15	0.52	−46.8	7.90	0.06	−46.3	7.70
500	2.14	−42.7	8.12	1.65	−42.2	8.06
1000	6.24	−37.0	8.26	5.74	−36.5	8.24

[a] The standard state is an ideal gas at 1 atm = 101 325 Pa pressure.

[b] The parameter x denotes either 1 or 2 (the partial processes) or T (the overall process).

magnitude than those considered [34] to be deviations for the simpler species studied using the conventional RRHO treatment.

Recently, it has been shown [8] that distinct maxima in the $\delta C_{p,1}^{\text{iso}}$ terms indicate an especially rapid interchange of relative stabilities of isomers. This appears to be the case with the system studied here. Temperature maxima occur at the temperatures 59.2 K (the height of the maximum is 14.2 J K^{-1} mol^{-1}) and 51.7 K (the height of the maximum is 14.3 J K^{-1} mol^{-1}) for the SCF and CPF approaches respectively. As a rule [8] these maxima appear before equimolarity is reached (see Table 2).

Finally, let us turn to the values of the partial and overall terms of the reactions (1)–(3) as presented in Table 4. There are no substantial qualitative differences between the two approximations studied. Again the heat capacity terms are interesting. From Table 4 it can be seen that although the partial terms $\Delta C_{p,i}^{\ominus}$ exhibit a smooth increase with temperature, the overall term $\Delta C_{p,\text{T}}^{\ominus}$ shows not only a local maximum, but also, at higher temperatures, a local minimum.

CONCLUDING REMARKS

The study of the thermodynamics of the system HF–Cl_2(g) shows that the two isomers forming this system exhibit considerable temperature mobility. This leads to a very low temperature at which equimolarity is attained. Thus the non-hydrogen-bonded structure is predominant at very low temperatures, whereas the hydrogen-bonded structure predominates at higher temperatures. This mutual temperature interplay also causes a marked enhancement of the heat capacity term. This is demonstrated in the (in principle) observable temperature dependence of the $\Delta C_p^{\ominus}$ term by a distinct maximum which potentially provides experimental proof of the existence of this isomerism. These features should be maintained in a qualitative sense even after transition to more realistic models [35,36] which provide a higher degree of non-rigidity and anharmonicity than the conventional RRHO model.

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