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Gaseous Complexes of Nickel Chloride with Aluminum Chloride and Gallium Chloride

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The thermodynamic functions ΔH and ΔS of the reactions (A) $NiCl_2(s) + LCl_3(g) = NiLCl_5(g)$ and (B) $NiCl_2(s) + L_2Cl_6(g) = NiL_2Cl_8(g)$ (L = Al, Ga) have been determined by spectrophotometry of the gas phase from 300 to 840 °C and by quenching of the equilibrated gas phase and analysis of the condensates. From combination of the results with a previous study where L = In it is found that ΔS does not depend significantly on L but is approximately 70 J mol^{-1} K^{-1} for reaction A and approximately 43 J mol^{-1} K^{-1} for reaction B. For reaction A ΔH is most positive for L = Ga, making the Ga complexes the least stable ones of the series where L = Al, Ga, In. This stability sequence follows the dimerization energies of LCl_3. The observed trend of the thermodynamic functions and the similarity of the spectra suggest that the structures of all $NiLCl_5$ complexes on one hand and of all the NiL_2Cl_8 complexes on the other hand are similar.

The formation of gaseous complexes between di- and trivalent metal halides can be described by equilibrium 1. In

$$\begin{gathered} MX_2(s) + nLX_3(g) = ML_nX_{3n+2}(g) \\ M = \text{alkaline-earth metal, transition metal} \\ L = Al, Ga, In, Fe, Sc \qquad X = Cl^-, Br^-, I^- \\ n = 1, 2, 3\ (4) \end{gathered} \tag{1}$$

most cases the dominating equilibrium is that with $n = 2$. According to Dewing,[1] this is the case in the $NiCl_2(s)/AlCl_3(g)$ system, where only $NiAl_2Cl_8(g)$ had been observed. But in the $NiCl_2(s)/InCl_3(g)$ system, it has been found[2] that $NiInCl_5(g)$ ($n = 1$) is the most important gaseous complex. It is therefore of interest to know whether the gaseous complexes of $NiCl_2$ with $GaCl_3$ are intermediate between those with $AlCl_3$ and $InCl_3$, i.e., whether they are one of the rare examples where both equilibria, one with $n = 1$ and the other with $n = 2$, can be conveniently studied. Such examples are important in the understanding of the thermodynamics of the stepwise formation of gaseous complexes.[5]

Evidence for the existence of gaseous complexes in the $NiCl_2/GaCl_3$ system has been given by Schäfer et al.,[6] but no quantitative studies have been performed so far. Dewing's investigation of the $NiCl_2(s)/AlCl_3(g)$ system was part of a pioneering survey[1] and therefore not intended to be of ultimate accuracy. Furthermore, recent results of chemical transport experiments by Schäfer[3] could not be reconciled with Dewing's values for the enthalpy and entropy of formation of $NiAl_2Cl_8(g)$. It therefore seemed worthwhile to reinvestigate the formation of gaseous complexes between $NiCl_2$ and $AlCl_3$.

Experimental Section

Chemicals. $NiCl_2$ was prepared by dehydrating the hydrated salt under vacuum and then subliming it in an evacuated quartz ampule. $AlCl_3$ (reagent grade, Fluka) was purified by sublimation under vacuum several times. $GaCl_3$ (prepared from 99.9% Ga) was by courtesy of Alusuisse and was used without further purification.

Analysis. Al and Ga where analyzed by atomic absorption for small concentrations and by EDTA titration for large concentrations. The volume of ampules and spectrophotometric cells was calculated from the weight of water they could contain.

Methods of Investigation. High-temperature spectroscopy and quenching experiments have been discussed previously.[4,5]

Computation. For the dissociation constants of $L_2X_6(g)$ and the vapor pressure of $NiCl_2$, literature data have been used:

$$Al_2Cl_6:\ \log\,[K_{diss}\,(\text{bar})] = 6.655 - 5684/T - 160700/T^2 \tag{2}$$ [25]

$$Ga_2Cl_6:\ \log\,[K_{diss}\,(\text{bar})] = 7.072 - 4595/T \tag{3}$$ [7]

$$NiCl_2:\ \log\,[P_{NiCl_2}\,(\text{bar})] = 10.136 - 12420/T \tag{4}$$ [2]

The optical absorbance of the gas phase of our systems is given in eq 5, m = monomer LCl_3, d = dimer L_2Cl_6, c = complex, c,m =

$$A = \epsilon_{NiCl_2}\frac{n_{NiCl_2}l}{V} + \epsilon_{c,m}\frac{n_{c,m}l}{V} + \epsilon_{c,d}\frac{n_{c,d}l}{V} \tag{5}$$

$NiLCl_5$ (complex with a monomer LCl_3), c,d = NiL_2Cl_8 (complex with a dimer L_2Cl_6), V = volume of the spectrophotometric cell, l = optical path length of the cell (10 cm in all experiments), n = number of moles, and ϵ = molar absorptivity (M^{-1} cm^{-1}). The first term in eq 5 is easy to calculate so long as there is solid $NiCl_2$ present (eq 4 and ϵ_{NiCl_2} from ref 2 and 8). It is negligibly small below 600 °C. Depending upon temperature, $AlCl_3$ pressure, and wavelength, the second and third terms contribute appreciably to A.

The number of moles of nickel in a cell is

$$n_{Ni} = n_{NiCl_2(s)} + n_{NiCl_2(g)} + n_{NiLCl_5(g)} + n_{NiL_2Cl_8(g)} \tag{6}$$

In all experiments only a small fraction of the LCl_3 is used to form gaseous complexes, and therefore only the first and second terms in eq 7 are important. Nevertheless, the third and fourth terms are taken into account, at least approximately (see below).

$$n_L = n_{LCl_3} + 2n_{L_2Cl_6} + n_{c,m} + 2n_{c,d} \tag{7}$$

Usually, the absorbance vs. temperature graph has a break when the solid phase, $NiCl_2$, disappears (e.g., Figure 3), but at the temperature of the break the vapor pressure of $NiCl_2$ is still given by eq 4. At this temperature the second term in eq 6 and the first term in eq 5 can be calculated as mentioned above. For the determination of the molar absorptivity of a gaseous complex the second and third term of eq 5 have to be determined simultaneously. This is feasible if the experimental conditions can be chosen so that the absorbance of one complex strongly prevails at the break temperature.

For the determination of the equilibrium constants of reaction 1, $K_{c,m} = P_{c,m}/P_m$ and $k'_{c,d} = P_{c,d}/P_m^2$, P_m is calculated from the amount of LCl_3 in the cell by using the law of ideal gases, $K_{diss}(L_2Cl_6)$ and eq 7. The calculation of $P_{c,m}$ or $P_{c,d}$ from the absorbance is straightforward if only one of the two complexes absorbs light; otherwise approximations have to be used.

The enthalpy and entropy of reaction 1 were calculated from the temperature dependence of the equilibrium constants (second law). ΔH and ΔS (and in some cases ϵ) were fitted individually or simultaneously so that the optical absorbances calculated with these parameters and the constants of the cell gave a best fit to the observed absorbances.[9] The error limit given is twice the standard deviation;

(1) E. W. Dewing, *Metall. Trans.*, **1**, 2169 (1970).
(2) F. Dienstbach and F. P. Emmenegger, *Inorg. Chem.*, **16**, 2957 (1977).
(3) H. Schäfer and J. Nowitzki, *Z. Anorg. Allg. Chem.*, **457**, 13 (1979).
(4) A. Dell'Anna and F. P. Emmenegger, *Helv. Chim. Acta*, **58**, 1145 (1975).
(5) F. Dienstbach and F. P. Emmenegger, *J. Inorg. Nucl. Chem.*, **40**, 1299 (1978).
(6) H. Schäfer, M. Binnewies, W. Domke, and J. Karbinski, *Z. Anorg. Allg. Chem.*, **403**, 116 (1974).
(7) W. Fischer and O. Jübermann, *Z. Anorg. Allg. Chem.*, **227**, 227 (1936).
(8) C. W. DeKock and D. M. Gruen, *J. Chem. Phys.*, **44**, 4387 (1966).
(9) C. Daul and J. J. Goel, *J. Chem. Soc., Faraday Trans. 1*, **73**, 985 (1977).

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Table I. Samples for the Visible Spectroscopy of $NiAlCl_5(g)$ and $NiAl_2Cl_8(g)$

sample	V, cm³	amt, mmol		T, °C	$SiCl_4$
		$NiCl_2$	$AlCl_3$		
1	29.05	9.95×10^{-3}	2.61	460–650	no
2	30.23	15.9×10^{-3}	4.33	427–506	no
3	30.23	13.5×10^{-3}	1.43	461–557	yes
4	30.15	16.3×10^{-3}	2.94	405–550	yes
5	28.12	14.3×10^{-3}	0.315	300–838	yes
6	27.87	6.79×10^{-3}	0.304	402–850	yes

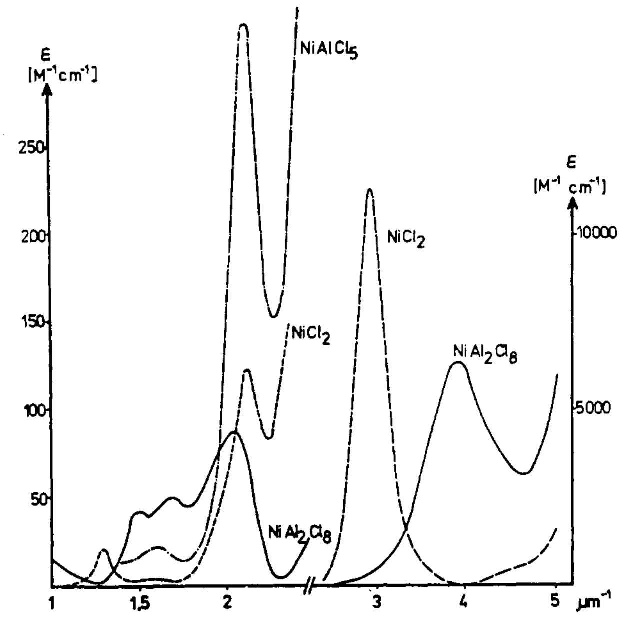


Figure 1. UV–visible spectra of $NiCl_2(g)$ (UV from ref 8), $NiAlCl_5(g)$, and $NiAl_2Cl_8(g)$ (from ref 10).

systematic errors are not considered.

Results

$NiCl_2/AlCl_3$. Dewing[1] investigated equilibrium 1a by en-

$$NiCl_2(s) + 2AlCl_3(g) = NiAl_2Cl_8(g) \qquad (1a)$$

trainment measurements in the range $P = 0.3–2$ bar and $T = 400–600$ °C. The UV–visible spectrum of $NiAl_2Cl_8(g)$ at 750 K has been published by Papatheodorou.[10] When we heated $NiCl_2$ and $AlCl_3$, the quartz windows of our optical cells were severely attacked at temperatures above ~700 K. With use of a hint from Schäfer,[11] this quartz attack could be completely suppressed by adding about 100 mg of $SiCl_4$ to a 30-cm³ optical cell (no influence of $SiCl_4$ on the spectra of the gaseous $NiCl_2/AlCl_3$ complexes could be detected). With samples containing a rather large amount of $AlCl_3$ (example no. 4 of Table I), we were able to reproduce Papatheodorou's spectrum of $NiAl_2Cl_8(g)$, but with samples containing less $AlCl_3$ (examples no. 5 and 6, Table I), the spectrum corresponded to that of $NiInCl_5(g)$.[2] We therefore concluded that $NiAl_2Cl_8(g)$ was the dominant gaseous complex at low temperatures and high aluminum chloride pressures while $NiAlCl_5(g)$ would prevail at elevated temperatures and smaller aluminum chloride pressures. The spectra of the gaseous nickel-containing species in the $NiCl_2/AlCl_3$ system are shown in Figure 1.

Formation of $NiAl_2Cl_8(g)$. The absorbances at 1.7 and 3.95 μm^{-1} are characteristic of $NiAl_2Cl_8(g)$ (Figure 1). In the temperature range of 450–550 °C, $K(8)$ was calculated from the absorbance of sample 4 at 1.7 μm^{-1}, while the absorbance

(10) G. N. Papatheodorou, *J. Phys. Chem.*, **77**, 472 (1973).
(11) H. Schäfer, *Z. Anorg. Allg. Chem.*, **445**, 129 (1978).

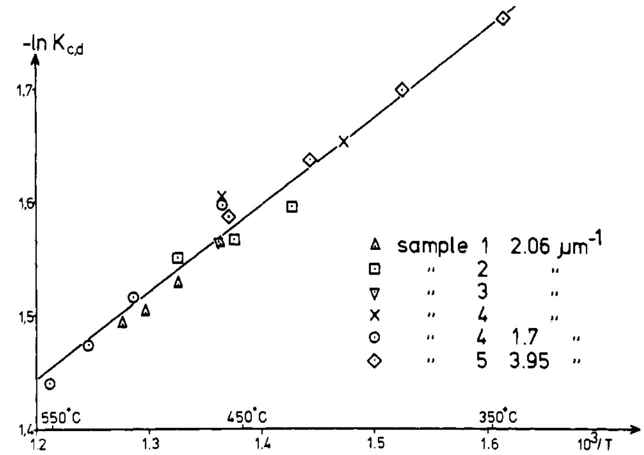


Figure 2. ln $(P_{NiAl_2Al_8}/P_{Al_2Cl_6}) = f(1/T)$. Sample numbers refer to Table I.

of sample 5 at 3.95 μm^{-1} was used to calculate $K(8)$ at temperatures from 300 to 490 °C. (It should be mentioned that

$$NiCl_2(s) + Al_2Cl_6(g) = NiAl_2Cl_8(g) \qquad (8)$$

$K(1a) = K(8)/K_{diss(Al_2Cl_6)}$.) The temperature dependence of $K(8)$ was used to calculate preliminary values of ΔH and ΔS of reaction 8. They were needed to estimate how much equilibrium 8 interferes in the evaluation of samples dominated by equilibrium 9.

In samples 1–4, at low temperatures, the absorbance at 2.06 μm^{-1} is mostly due to $NiAl_2Cl_8(g)$, but the absorbance of $NiAlCl_8(g)$ is not negligible. When ΔH and ΔS of reaction 9 were known (see below), the absorbance of $NiAlCl_5(g)$ in samples 1–4 could be calculated, and if it was less than 10% of the total absorbance, the data were used to calculate $K(8)$. All the ln $K(8)$ from evaluation at 1.7, 2.06, and 3.95 μm^{-1} are shown in Figure 2. Considering the range of temperature (350–550 °C) and pressure (1.3–4.2 bar of $Al_2Cl_6(g)$), the linearity of the ln K vs. $1/T$ plot is satisfactory. From a linear least-squares fit it follows that at 450 °C $\Delta H(8) = 62.8 \pm 2.5$ kJ mol⁻¹ and $\Delta S(8) = 38.1 \pm 3.8$ J mol⁻¹ K⁻¹. In order to verify the result of the optical investigation by an independent method, we performed three quenching experiments at 400 °C. They yielded $K(8) = (1.6 \pm 0.4) \times 10^{-3}$, while with $\Delta H(8)$ and $\Delta S(8)$ from optical measurements, $K(8) = 1.3 \times 10^{-3}$ is obtained. Considering the large error generally associated with quenching experiments, the agreement is satisfactory.

Formation of $NiAlCl_5(g)$. The equilibrium constants of reactions 9 and 9a are related to each other: $K(9) =$

$$NiCl_2(s) + AlCl_3(g) = NiAlCl_5(g) \qquad (9)$$

$$NiCl_2(s) + {}^1/_2Al_2Cl_6(g) = NiAlCl_5(g) \qquad (9a)$$

$K(9a)[1/K_{diss(Al_2Cl_6)}{}^{1/2}]$. For convenience we will evaluate our measurements according to equilibrium 9.

Sample 5 contains only a little aluminum chloride, and its absorbance at 2.1 μm^{-1} is therefore almost entirely due to $NiCl_2(g)$ and $NiAlCl_5(g)$ and not to $NiAl_2Cl_8(g)$. The break in the absorbance vs. temperature graph (Figure 3) is due to the disappearance of the solid-phase $NiCl_2$, and the decrease of the absorbance above this temperature is caused by reaction 10 (at 2.1 μm^{-1}: $\epsilon_{NiCl_2} < \epsilon_{NiAlCl_5}$, see Figure 1). At 760 °C,

$$NiAlCl_5(g) = NiCl_2(g) + AlCl_3(g) \qquad (10)$$

the temperature of the break, the composition of the gas phase is $n_{NiCl_2} = 4.24 \times 10^{-6}$, $n_{NiAlCl_5} = 9.98 \times 10^{-6}$, and $n_{NiAl_2Cl_8} = 0.051 \times 10^{-6}$, from which $\epsilon_{NiAlCl_5} = 319$ M⁻¹ cm⁻¹ at 2.1 μm^{-1}. With this value for ϵ_{NiAlCl_5}, $K(9)$ is determined from the increasing (550–750 °C) and $K(10)$ from the decreasing

Table II. Enthalpy (kJ mol^{-1}) and Entropy (J mol^{-1} K^{-1}) of Formation of $NiLCl_5(g)$ and $NiL_2Cl_8(g)$ at 298 K

(A) $NiCl_2(s) + LCl_3(g) = NiLCl_5(g)$ $C_p = -6$ J mol^{-1} K^{-1} [a]
(B) $NiCl_2(s) + L_2Cl_6(g) = NiL_2Cl_8(g)$ $C_p = -4$ J mol^{-1} K^{-1} [a]
(C) $CoCl_2(s) + L_2Cl_6(g) = CoL_2Cl_8(g)$ (for Comparison)

	L					
	Al		Ga		In[b]	
eq	ΔH°_{298}	ΔS°_{298}	ΔH°_{298}	ΔS°_{298}	ΔH°_{298}	ΔS°_{298}
A	98.8 ± 2.5	72.1 ± 2.5	108.8 ± 2.5	67.4 ± 2.1	93.7 ± 8.4	67.7 ± 8.4
B	64.5 ± 2.9[c]	41.6 ± 4.2[c]	70 ± 8	42[a]	77.4 ± 8.4	45.2 ± 8.4
C	46.4[d]	46.2[d]	45.6[e]	40.2[e]	49.5[f]	43.5[f]

[a] Estimated value. [b] Reference 2. [c] Reference 1: $\Delta H = 51.9$, $\Delta S = 37.7$. [d] Reference 1, 4, and 24. [e] Reference 12 and 22. [f] References 2, 18, and 23.

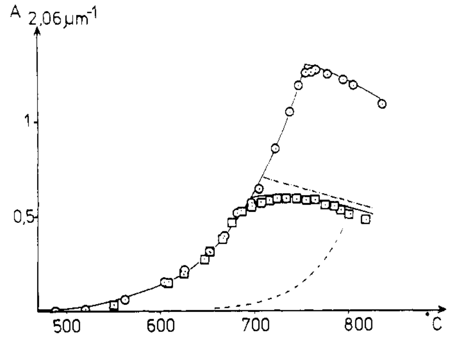


Figure 3. Temperature dependence of the absorbance due to the formation and decomposition of gaseous $NiCl_2/AlCl_3$ complexes: (○) sample 5; (□) sample 6; (—) absorbance calculated with thermodynamic values of Table II and $\epsilon_{NiAlCl_5} = 319$ M^{-1} cm^{-1}, $\epsilon_{NiCl_2} = 117$ M^{-1} cm^{-1}, $\epsilon_{NiAl_2Cl_8} = 80$ M^{-1} cm^{-1} at 2.1 μm^{-1}; (–·–) absorbance of sample 6 neglecting formation of $NiAl_2Cl_8(g)$; (---) absorbance of $NiCl_2(g)$ in equilibrium with $NiCl_2(s)$.

(760–840 °C) absorbance. $K(9)$ and $K(10)$ are related to each other by $\Delta G(10) = \Delta G_{subl(NiCl_2)} - \Delta G(9)$.

Under the experimental conditions of sample 5, equilibrium 11 can be neglected. In sample 6 the ratio of aluminium

$$NiAl_2Cl_8(g) = NiAlCl_5(g) + AlCl_3(g) \qquad (11)$$

chloride to nickel chloride is larger than in sample 5, and therefore equilibrium 11 has to be considered ($\Delta G(11) = \Delta G(9) + \Delta G_{diss(Al_2Cl_6)} - \Delta G(8)$).

The joint evaluation of samples 5 and 6 yields $\Delta H(9) = 94.8 \pm 2.5$ kJ mol^{-1} and $\Delta S(9) = 65.0 \pm 2.5$ J mol^{-1} K^{-1} at $T_{av} = 940$ K. If we combine $\Delta G(8)$, $\Delta G(9)$, ϵ_{NiAlCl_5}, and $\epsilon_{NiAl_2Cl_8}$ with literature values for $\Delta G_{subl(NiCl_2)}$ and $\Delta G_{diss(Al_2Cl_6)}$ to calculate the absorbance vs. temperature in our samples 5 and 6, the agreement between calculated and measured absorbance is quite satisfactory (Figure 3).

$NiCl_2/GaCl_3$. Formation of $NiGa_2Cl_8(g)$. As expected, the stability of $NiGa_2Cl_8$ is low,[12,13] but it was not anticipated that its spectrum would be masked by the spectrum of $NiGaCl_5$. As this was the case, it was not possible to determine the equilibrium constant of eq 12 by optical spectroscopy but only

$$NiCl_2(s) + Ga_2Cl_6(g) = NiGa_2Cl_8(g) \qquad (12)$$

by quenching experiments, which are not very accurate. At 400 °C we obtained $K(12) = 5.24 \times 10^{-3}$. With an estimated entropy value[12,14] of $\Delta S(12) = 46$ J mol^{-1} K^{-1}, we obtained $\Delta H(12) = 70$ kJ mol^{-1}.

Formation of $NiGaCl_5(g)$. Equilibrium 13 could be investigated by optical spectroscopy. The samples are described

$$NiCl_2(s) + GaCl_3(g) = NiGaCl_5(g) \qquad (13)$$

(12) F. P. Emmenegger, *Inorg. Chem.*, **16**, 343 (1977).
(13) J. W. Hastie, "High Temperature Vapors", Academic Press, New York, 1975, pp 126–147.
(14) H. Schäfer, *Angew. Chem., Int. Ed. Engl.*, **15**, 713 (1976).

Table III. Samples for the Visible Spectroscopy of $NiGaCl_5(g)$

		amt, mol	
sample	V, cm^3	$NiCl_2$	$GaCl_3$
1	34.99	1.47×10^{-5}	1.29×10^{-3}
2	33.70	excess	1.10×10^{-3}
3	33.17	4.45×10^{-6}	1.10×10^{-3}
4	38.98	1.39×10^{-5}	1.41×10^{-3}

Table IV.[a] Thermodynamics of $^1/_2Ni_2Cl_4(g) + {}^1/_2L_2Cl_6(g) = NiLCl_5(g)$

	Al	Ga	In[b]
ΔH°_{298}, kJ mol^{-1}	−13.0	−18.8	−15.5
ΔS°_{298}, J mol^{-1} K^{-1}	−0.8	−6.7	−7.5

[a] Thermodynamic values used to convert values of Table II, eq A, into values of Table IV (ΔH_{298} in kJ mol^{-1}, ΔS_{298} in J mol^{-1} K^{-1}): $NiCl_2(s) \rightarrow NiCl_2(g)$, 247.2, 216.3;[2] $2NiCl_2(g) \rightarrow Ni_2Cl_4(g)$ −144.8, −133.9;[17] $2AlCl_3(g) \rightarrow Al_2Cl_6(g)$ −126.5, −153.1;[19] $2GaCl_3(g) \rightarrow Ga_2Cl_6(g)$ −94.6, −150.6;[7,17] $2InCl_3(g) \rightarrow In_2Cl_6(g)$ −131.4, −152.3.[20] [b] Reference 2.

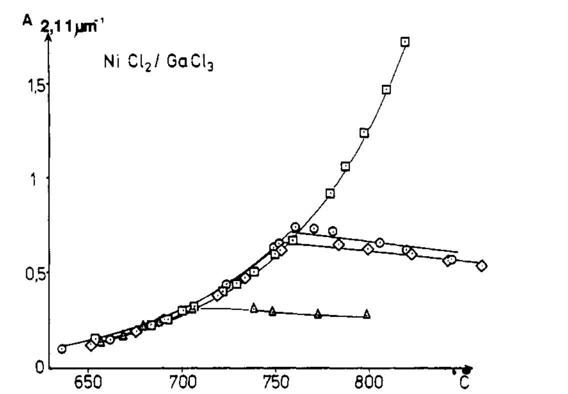


Figure 4. Temperature dependence of the absorbance due to the formation and decomposition of $NiCl_2/GaCl_3$ complexes: (○) sample 1, (□) sample 2, (△) sample 3, (◇) sample 4 (sample numbers refer to Table III); (—) absorbance calculated with the thermodynamic values of Table II and $\epsilon_{NiGaCl_5} = 215$ M^{-1} cm^{-1}, $\epsilon_{NiCl_2} = 117$ M^{-1} cm^{-1}.

in Table III. The spectrum of $NiGaCl_5(g)$ is similar to those of $NiAlCl_5(g)$ and $NiInCl_5(g)$,[2] with a peak at 2.11 μm^{-1}. The molar absorptivity, $\epsilon_{2.11\mu m^{-1}} = 215$ M^{-1} cm^{-1}, was calculated from the (extrapolated) maximum of absorbance in the A vs. T graph (Figure 4) of samples 1 and 4. In deriving $K(13)$ from absorbance measurements at 2.11 μm^{-1}, the formation of $NiGa_2Cl_8$ was taken into account (although it was unimportant) by using the approximate ΔH and ΔS values mentioned above and an estimated molar absorptivity of 80 M^{-1} cm^{-1} in analogy to the molar absorbtivity of $NiAl_2Cl_8(g)$. We find $\Delta H(13) = 104.4 \pm 2.4$ kJ mol^{-1} and $\Delta S(13) = 60.2 \pm 2.1$ J mol^{-1} K^{-1} at $T_{av} = 1020$ K.

Table V. Stepwise Formation of Gaseous Complexes

reaction	L = Al		L = Ga		L = In[a]	
	$-\Delta H°_{298}$, kJ mol^{-1}	$-\Delta S°_{298}$, J mol^{-1} K^{-1}	$-\Delta H°_{298}$, kJ mol^{-1}	$-\Delta S°_{298}$, J mol^{-1} K^{-1}	$-\Delta H°_{298}$, kJ mol^{-1}	$-\Delta S°_{298}$, J mol^{-1} K^{-1}
$NiCl_2(g) + LCl_3(g) = NiLCl_5(g)$	148.5	144.3	138.5	149.0	156.9	150.2
$NiLCl_5(g) + LCl_3(g) = NiL_2Cl_8(g)$	160.2	183.3	129.7	176.1	144.3	166.5
average	154.4 ± 5.9		134.1 ± 4.4		150.6 ± 6.3	

[a] Reference 2.

Discussion

$NiAlCl_5$(g). $NiAlCl_5$(g) has been observed by Binnewies[15] in the mass spectrometer. If we use his published ion intensities to calculate $K(9)$, we obtain $K(9)_{893K} = 8.5 \times 10^{-3}$, while our measurements yield $K(9)_{893K} = 9.9 \times 10^{-3}$. Considering the limited accuracy of the two methods of investigation, the agreement is excellent but perhaps somewhat fortuitous.

$NiAl_2Cl_8$. For equilibrium 8 (B in Table II), our thermodynamic data are rather different from those of ref 1; e.g., at 773 and 873 K our $K(8)$ is more than five times smaller than that of ref 1. Schäfer[3] transported $NiCl_2$(s) with Al_2Cl_6(g) from 736 to 676 K and observed a transport rate of $(0.36 \pm 0.07) \times 10^{-5}$ mol h^{-1}. The predicted transport rate computed with the thermodynamic data of ref 1 is around five times larger, $(2 \pm 0.3) \times 10^{-5}$ mol h^{-1}, while with our thermodynamic data it is $(0.39 \pm 0.06) \times 10^{-5}$ mol h^{-1}, in good agreement with the experimental value.

The contribution of equilibrium 9 to this chemical transport is less than 10%, and therefore the agreement between calculated and observed transport rate mainly concerns our data of equilibrium 8.

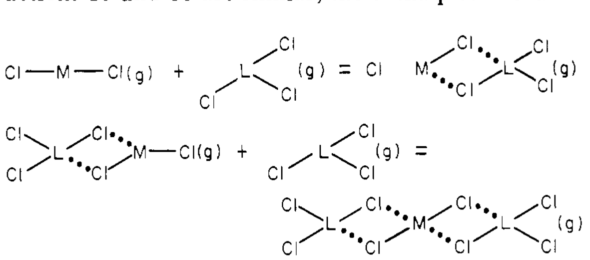
Thermodynamics and Structures. For an interpretation of the thermodynamics of the formation of gaseous metal halide complexes, various models have been proposed, and our results shall be checked against them.

(a) The entropy and enthalpy of reaction 14 are approximately zero.[13,14]

$$^1/_2(NiCl_2)_2(g) + {}^1/_2(LCl_3)_2(g) = NiLCl_5(g) \quad (14)$$

A small negative enthalpy value could be rationalized by the reduction of the cation–cation repulsion energy.[13] To calculate the enthalpy and entropy of reaction 14, one relies on the data for the evaporation and dimerization of nickel chloride, which are both known only to ca. ±8 kJ mol^{-1} and 8 J mol^{-1} K^{-1}, respectively.[16,17] Considering this source of uncertainty, our results agree reasonably well with the condition set by equilibrium 14 (see Table IV).

(b) Because the number and type of bonds formed in reactions 15 and 16 are similar, the enthalpies of reactions 15 and 16 should be similar.[5,12]



(15)

(16)

The entropies of these reactions will depend little on the masses of L and M, and they have been estimated[5,18] to be $\Delta S(15) = -150$ J mol^{-1} K^{-1} and $\Delta S(16) = -170$ J mol^{-1} K^{-1}. So far, most examples used to illustrate this scheme of stepwise formation of gaseous complexes have been complexes with indium chloride, but the complexes of nickel chloride with aluminum and gallium chloride fit as well (Table V). It should be mentioned that according to this model, the relative thermodynamic values of reactions 15 and 16 are not altered if MLX_5(g) contains a fourfold coordinated M (trigonal pyramid) and ML_2X_8(g) a sixfold coordinated M (octahedron).

(c) In a recent review, Schäfer emphasizes the importance of changing (or maintaining) the coordination number of M in the course of the formation of gaseous metal halide complexes.[21] In reaction 17, the change of coordination M suffers

$$MCl_2(s) + L_2Cl_6(g) = ML_2Cl_8(g) \quad (17)$$

in going from the solid to the gaseous phase does not depend on L. Therefore, the thermodynamic functions of reaction 17 should, for a given M, be rather independent of L. The complexes of $CoCl_2$ have so far been the only ones where the stability with all three group 3 chlorides ($AlCl_3$, $GaCl_3$, and $InCl_3$) have been known, and these results are included in table II for comparison. Considering the limited accuracy of our data (estimated ΔS) for the formation of $NiGa_2Cl_8$(g) and

Table VI. Stability of NiL_2Cl_8(g) and $NiLCl_5$(g) at 900 K

	Al	Ga	In
$K(17) = P_{c,d}/P_d$	2.2×10^{-2}	1.1×10^{-2}	0.6×10^{-2}
$K(1a) = P_{c,d}/P_m{}^2$	1.8×10^{3}	1.2×10^{1}	6.4×10^{2}
$K(9) = P_{c,m}/P_m$	7.8×10^{-3}	1.2×10^{-3}	9.1×10^{-3}
$\Delta H_{dim(LCl_3)}$[a]	−127	−95	−131

[a] kJ mol^{-1}; see Table IV.

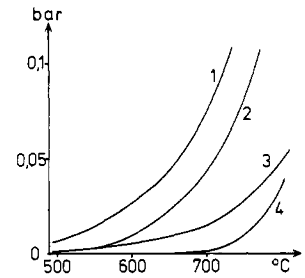


Figure 5. Total pressure of nickel complexes in an ampule containing 1 mol of LCl_3/22.4 L and excess $NiCl_2$: 1, $NiAlCl_5 + NiAl_2Cl_8$; 2, $NiInCl_5 + NiIn_2Cl_8$; 3, $NiGaCl_5 + NiGa_2Cl_8$; 4, $NiCl_2$ for comparison.

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$NiIn_2Cl_8(g)$, the hypothesis that equilibrium 17 does not depend on L seems to be supported by the nickel complexes (Table II).

If we calculate $K(17)$ at, e.g., 900 K using the thermodynamic functions of Table II, we find that the values differ by less than 1 order of magnitude (Table VI) and that $K_{NiAl_2Cl_8} > K_{NiGa_2Cl_8} > K_{NiIn_2Cl_8}$. This, however, does not imply that the partial pressure of the gaseous nickel complexes in an ampule containing solid nickel chloride and identical amounts of LCl_3 is proportional to these equilibrium constants. To illustrate the relative stability of NiL_2Cl_8, it is better to compare the reactions $NiCl_2(s) + 2LCl_3(g) = NiL_2Cl_8(g)$, which show that the stability of $NiL_2Cl_8(g)$ is roughly proportional to the dimerization energy of $LCl_3(g)$. The same trend is observed for the formation of $NiLCl_5(g)$. This is expected if the approximations discussed in the context of eq 15 and 16 are valid. The relative amounts of nickel carried into the gas phase under "reasonable" experimental condition are shown in Figure 5.

Schäfer[21] and Dewing[1] proposed that the thermodynamics of reaction 17 should be similar ($\Delta H = 50 \pm 8$ kJ mol^{-1}, $\Delta S = 46 \pm 13$ J mol^{-1} K^{-1}) for all M which have octahedral coordination in the solid MCl_2 as well as in the gaseous complex. While the enthalpies of formation of the cobalt complexes fit into this scheme, the enthalpies of the nickel complexes do not—they are too positive (Table II). Within Schäfer and Dewing's concept this would be understandable if the coordination number of the nickel was smaller in the gas than in the solid. This, however, is contradicted by the UV–visible spectrum, which is essentially that of a $NiCl_6$ chromophore[10] with only a small—if any—contribution from a tetrahedral $NiCl_4$ center. Although we have no proposition for reconciling the low stability of the $NiL_2Cl_8(g)$ complexes with the structure derived from their optical spectrum, we consider it worth mentioning that $NiCl_2$ has by far the highest melting point (1000 °C) of all the isostructural chlorides ($CdCl_2$-type) for which equilibrium 17 has been studied (e.g., $MnCl_2$, 650 °C; $CoCl_2$, 740 °C). The structural stability which is responsible for the high melting point of $NiCl_2$ evidently also is against its "evaporation" by equilibrium 17.

The results of the present investigation of the stability of $NiAlCl_5(g)$, $NiAl_2Cl_8(g)$, $NiGaCl_5(g)$, and $NiGa_2Cl_8(g)$ are largely consistent with the ideas about the correlation between stability and structure of gaseous complexes. This agreement with the general aspects of a larger experimental body of gaseous complexes is considered as an additional element of support for our results.

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Note Added in Proof. While this paper was in press, a paper dealing with the stability of $NiAl_2Cl_8(g)$ and $NiAl_3Cl_{11}(g)$ has been published by W. Lenhard and H. Schäfer, *Z. Anorg. Allg. Chem.*, **482**, 167 (1981).

Registry No. $NiCl_2$, 7718-54-9; $AlCl_3$, 7446-70-0; $GaCl_3$, 13450-90-3; $NiAlCl_5$, 81315-93-7; $NiGaCl_5$, 66143-12-2; $NiAl_2Cl_8$, 40556-06-7; $NiGa_2Cl_8$, 66594-41-0; Al_2Cl_6, 13845-12-0; Ga_2Cl_6, 15654-66-7.

Contribution from Rocketdyne, a Division of Rockwell International Corporation, Canoga Park, California 91304

Fluorine Perchlorate. Vibrational Spectra, Force Field, and Thermodynamic Properties

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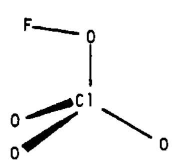
Infrared spectra of gaseous, solid, and matrix-isolated ClO_3OF and Raman spectra of liquid ClO_3OF are reported. All 12 fundamental vibrations expected for the covalent perchlorate structure



of symmetry C_s were observed and assigned. A modified valence force field was computed for ClO_3OF by using the observed ^{35}Cl–^{37}Cl isotopic shifts, symmetry relations between the A′ and the A″ block, and the off-diagonal symmetry force constants of the closely related $FClO_3$ molecule as constraints. Previous assignments for ClO_3OCl, ClO_3OBr, ClO_3OCF_3, Cl_2O_7, and Cl_2O_7 are revised. The ^{19}F NMR spectrum of ClO_3OF was recorded, and thermodynamic properties were computed in the range 0–2000 K.

Introduction

Fluorine perchlorate (or perchloryl hypofluorite) was probably first prepared[1] in 1929 by Fichter and Brunner by the fluorination of dilute $HClO_4$ with F_2 but was incorrectly identified. The first positive identification of ClO_3OF was reported[2] in 1947 by Rohrback and Cady, who obtained the compound from the reaction of F_2 with concentrated perchloric acid. They reported that ClO_3OF consistently exploded when frozen.

In view of its explosive nature, it is not surprising that very few papers dealing with ClO_3OF have been published since then. In 1962, Agahigian and coworkers reported[3] the ^{19}F NMR spectrum of ClO_3OF in $CFCl_3$ and four infrared absorptions of the gas. The same four infrared bands have also been observed in a study[4] at United Technology Corp. in which the heat of hydrolysis was measured for ClO_3OF. Macheteau and Gillardeau studied[5] the thermal decomposition of ClO_3OF

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