Neodymium Chloride–Aluminum Chloride Vapor Complexes[1]

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Abstract: The vaporization of solid $NdCl_3$ in the presence of Al_2Cl_6 gas has been studied spectrophotometrically in the range 500–900°K and 1–7 atm. Molar absorptivity of the strongest absorption peak at 17,030 cm^{-1} was found to be 18.8 l./(mole cm). At 800°K, the apparent vapor pressure of $NdCl_3$ is increased by a factor of 3×10^7 by the presence of 1 atm of Al_2Cl_6. The large increase in volatility is rationalized in terms of the formation of neodymium chloride–aluminum chloride vapor complexes according to the reactions $NdCl_3(s) + 1.5Al_2Cl_6(g) = NdAl_3Cl_{12}(g)$ and $NdCl_3(s) + 2Al_2Cl_6(g) = NdAl_4Cl_{15}(g)$. The equilibrium quotients for the two reactions were fitted to expressions of the form $\log K = A + (B/T)$ with $A_1 = 0.547$, $B_1 = -2353$, $A_2 = -2.711$, and $B_2 = -370$.

The existence and remarkable volatilities of vapor complexes between aluminum chloride and alkaline earth chlorides,[3,4] 3d transition metal dichlorides,[4] and representative 4f (neodymium trichloride)[5] and 5f (uranium tetrachloride) chlorides[6] have been recognized only in recent years. Thus, aluminum chloride has been shown to form gaseous complexes with metal chlorides widely distributed throughout the periodic table. A driving force for these reactions is the strong chloride ion affinity of $AlCl_3$ as exemplified in a recent study of solvation of $CoCl_2$ in $AlCl_3$-containing melts.[7]

In the present paper, the spectroscopic and thermodynamic properties of aluminum chloride–neodymium trichloride vapor complexes will be discussed.

Experimental Section

Method. The equilibrium

$$n_1\mathrm{NdCl_3(s)} + n_2\mathrm{Al_2Cl_6(g)} = \mathrm{Nd}_{n_1}\mathrm{Al}_{2n_2}\mathrm{Cl}_{3n_1+6n_2}\mathrm{(g)} \qquad \text{(I)}$$

was studied spectrophotometrically. Sealed quartz optical cells were used containing known amounts of $NdCl_3(s)$ and $AlCl_3(s)$. The amounts of $AlCl_3$ were adjusted so that all the $AlCl_3$ in the cell was in the vapor phase at 580°K and above. In the temperature range of the measurements, 600–900°K, the vapor pressure of pure $NdCl_3$ is very low[8] and $NdCl_3(g)$ does not contribute to the absorption of light. The measured optical densities in the visible region are therefore due only to the Nd complexes. Three types of experiments were carried out.

(a) It was ascertained that the solid phase present above 580°K was $NdCl_3$, not a compound between $NdCl_3$ and $AlCl_3$.

(b) The molar absorptivity at a given wavelength was determined from the relation

$$\epsilon_{\mathrm{Nd-Al-Cl}} = \frac{AV}{nl} \qquad (1)$$

where $\epsilon_{\mathrm{Nd-Al-Cl}}$ = molar absorptivity of one or a mixture of two or more gaseous neodymium chloride–aluminum chloride complexes, V = volume of cell (liters), A = absorbance at a given wavelength λ_i, n = moles of Nd-Al-Cl complexes in the gas phase as complex, and l = optical path length (cm). $\epsilon_{\mathrm{Nd-Al-Cl}}$ was determined for the ${}^4I_{9/2}$–${}^4G_{5/2}$ hypersensitive transition[9] which has an absorption maximum near 17,030 cm^{-1}.

(c) The partial vapor pressures of the complexes were determined by performing experiments similar to (b), but with excess $NdCl_3(s)$ always present in the cell. Measuring the absorbance at the same wavelength as for (b), the partial vapor pressure is given by

$$P_{\mathrm{Nd-Al-Cl}} = \frac{ART}{\epsilon_{\mathrm{Nd-Al-Cl}}\,l} \qquad (2)$$

In order to determine n_2 in eq I, a series of experiments with excess $NdCl_3(s)$ and varying $Al_2Cl_6(g)$ pressures was performed.

Procedure. $AlCl_3$ was prepared by passing HCl over analytical grade Al wire at about 500°K. The HCl, produced by treating H_2SO_4 with NaCl, was dried by passage through a trap cooled with an acetone–Dry Ice mixture. The $AlCl_3$ was sublimed in an HCl atmosphere, and HCl was pumped off under vacuum. $NdCl_3$ was prepared by dehydration of the hydrate with HCl, followed by vacuum sublimation at 1000°K.

The $NdCl_3$ and $AlCl_3$ were weighed out on a microbalance and transferred to an optical cell in a helium atmosphere drybox whose water content was <3 ppm.

In order to permit spectral measurements to be made over as large a temperature and pressure interval as possible, heavy-walled cylindrical cells (wall thickness 2–3 mm) and 20-cm path lengths were used, with volumes ranging between 50 and 80 cm^3. The cells were fabricated from fused silica tubes by fusing 3-mm thick fused silica windows within the ends of the cell body making sure that the entire window thickness was employed in making the seal. Several cells ruptured before this procedure in making the seals was adopted. The cells, after loading through a side arm, were sealed off under vacuum. Cell volumes were determined to within 0.2% by pycnometric weighing, and the path length was measured with a caliper to ±0.03 cm.

The cells were placed in a cylindrical furnace of a type previously described.[9] Spectra were generally measured in the temperature range 600–900°K and total pressures of 1–7 atm.

In order to prevent condensation of $AlCl_3$ or $NdCl_3$ on the windows, and to minimize heat losses, small auxiliary Pt heaters were placed in both end portions of the furnace, and the ends of the furnace were fitted with outer quartz windows. The voltage of the Pt heaters was kept constant over a run. With this arrangement, the temperature at the cell windows was about 40° higher than the middle of the cell at 500°K and only a few degrees higher at 900°K. Calibration curves for the temperature distribution along the cells were obtained as a function of temperature with a dummy cell in the furnace. In order to vary the position of the thermocouple within the cell, a small hole was drilled through the furnace and cell windows. Heat losses were found to be somewhat less during an actual run so that the average temperatures determined in the calibration runs are estimated to be within ±5° of the actual temperature.

During the runs, the temperature was measured with the thermocouple situated near the middle of the furnace adjacent to the cells.

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Table I. Determination of Molar Absorptivity ϵ for Nd–Al–Cl as Complex at 17,030 Cm^{-1} for the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ Transition[a]

Experiment	T_{min}, °K	$A_{Nd-Al-Cl}$	$\epsilon_{Nd-Al-Cl}$	$\bar{\epsilon}_{Nd-Al-Cl}$
A				
$P^0_{A_2iCl_6} = 1.019 \times 10^{-3}T$ atm	607.5	0.0377	16.9	17.0
$w_{NdCl_3} = 1.515 \times 10^{-3}$ g	672.3	0.0390	17.5	
$V = 49.30 \times 10^{-3}$ l.	771.6	0.0392	17.6	
$l = 18.20$ cm	842.6	0.0375	16.8	
$\epsilon_{Nd-Al-Cl} = 448.1A_{Nd-Al-Cl}$ l./(mole cm)				
B				
$P^0_{Al_2Cl_6} = 4.934 \times 10^{-3}T$ atm	594.4	0.0269 ± 0.0005	18.53	18.5 ± 0.3
$w_{NdCl_3} = 1.407 \times 10^{-3}$ g	772.2	0.0267 ± 0.0005	18.39	
$V = 78.73 \times 10^{-3}$ l.				
$l = 20.36$ cm				
$\epsilon_{Nd-Al-Cl} = 688.7A_{Nd-Al-Cl}$ l./(mole cm)				
C				
$P^0_{Al_2Cl_6} = 9.514 \times 10^{-3}T$ atm	643.5	0.0889 ± 0.0010	18.86	19.0 ± 0.2
$w_{NdCl_3} = 4.576 \times 10^{-3}$ g	726.6	0.0894 ± 0.0010	18.97	
$V = 73.42 \times 10^{-3}$ l.	866.9	0.0905 ± 0.0010	19.20	
$l = 18.95$ cm				
$\epsilon_{Nd-Al-Cl} = 212.2A_{Nd-Al-Cl}$ l./(mole cm)				

[a] T_{min} = minimum temperature in cell in °K; $\bar{T}$ = average temperature in °K; $A_{Nd-Al-Cl} = \log (I^0/I)$ for the gaseous complexes at ~17,030 cm^{-1} taken as maximum above background curve; $\epsilon_{Nd-Al-Cl}$ = molar absorptivity of gaseous complexes for 17,030 cm^{-1}; $P_{Nd-Al-Cl}$ = pressure of the gaseous complexes; $P^0_{Al_2Cl_6}$ = pressure of Al_2Cl_6 assuming all $AlCl_3$ initially added to the cell to be in the gas phase and neglecting dissociation; $P_{Al_2Cl_6}$ = pressure of Al_2Cl_6 assuming all $AlCl_3$ in gas phase and correcting for dissociation to $AlCl_3$ and reaction with $NdCl_3$; w_{NdCl_3} = total amount of $NdCl_3$ in cell; V = volume of cell; l = optical path length of cell.

It was found that this temperature was within ±0.5° of the minimum temperature measured inside the cell during a calibration run.

A Cary 14 H spectrophotometer with the sequence light source → chopper → sample → monochromator → detector → ac amplifier → recorder was used for the spectral measurements. The usefulness of this arrangement for high-temperature measurements has been described.[10]

Two slide-wires were used covering absorbances from 0 to 0.2 and from 0 to 2.

Above 900°K, cell window attack resulted in severe scattering of the light beam, presumably due to the reaction

$$2Al_2Cl_6(g) + 3SiO_2(s) = 2Al_2O_3(s) + 3SiCl_4(g) \qquad \text{(II)}$$

The JANAF Tables[11] give for reaction II, $\Delta G° = -2.975$ kcal at 500°K and $\Delta G° = -3.295$ kcal at 1000°K. Despite favorable thermodynamics, the reaction does not occur to any significant extent below 900°K.

In one instance it was possible to perform measurements up to 1200°K (sample F) by heating the sample rapidly from 800 to 1200°K. Later, it was realized that reaction I is slow to reach equilibrium. For this reason, an equilibration time of at least 5 hr was allowed before making spectral measurements. Measurements above 900°K were not performed because of cell attack according to equilibrium II. The dissociative equilibrium

$$Al_2Cl_6(g) = 2AlCl_3(g) \qquad \text{(III)}$$

for which $K = 1$ at 882°K, results essentially in a doubling of the total pressure over a small temperature interval and constitutes an additional hazard for cell rupture.

An exact determination of light scattering could not be obtained because of variations in the optical characteristics of the cells and in the degree of attack on cell windows. Some of the scattering in later experiments (Figure 3) was caused by a slightly damaged mirror in the spectrophotometer. Difficulties in subtracting background scattering were further complicated by the low concentration and molar absorptivity of the neodymium complexes. Scattering corrections were finally made by fitting the background curve individually to regions of minimum absorption between peaks. The molar absorptivity was calculated from the difference between this curve and the peak height.

Results and Discussion

Solid Phase in Equilibrium with Gaseous Al_2Cl_6 above 600°K. In order to determine the nature of the solid phase in equilibrium with gaseous Al_2Cl_6, the following experiment was performed. $NdCl_3$ (0.03 g) and $AlCl_3$ (0.27 g) were sealed in an evacuated quartz tube whose volume was 26.5 cm^3. The tube was heated to 510°K in a nichrome wound Vycor tube furnace. At this temperature, solid $NdCl_3$ dissolved completely in liquid $AlCl_3$. The tube was then heated to 630°K where visual observation showed that only a solid phase was present at one end of the tube. The entire tube was held at this temperature for 6 hr to ensure equilibrium. The other end of the tube was then quenched in ice water causing condensation of $AlCl_3$ together with a small amount of $NdCl_3$. No change appeared to take place during this procedure in the solid phase originally present. The entire tube was then allowed to reach room temperature. The tube was opened and the solid phase containing most of the neodymium was identified as $NdCl_3$ by means of an X-ray diffraction powder pattern. On the basis of these observations, it was concluded that $NdCl_3$ does not form a crystalline complex with $AlCl_3$ under these conditions.[12]

Determination of Molar Absorptivity. Three different experiments were carried out in order to determine the molar absorptivity of the gaseous neodymium complex. The pertinent data are given in Table I. The cells were filled with small amounts (1–4 mg) of $NdCl_3$ to ensure that all of the $NdCl_3$ was in the vapor phase in the range 600–900°K in the presence of 1–9.5 atm of $AlCl_3$.

$\epsilon_{Nd-Al-Cl}$ is given for the absorption maximum at 17,030 ± 20 cm^{-1} with the main source of error for a given experiment arising from the determination of absorbance.

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(11) JANAF Thermochemical Data, The Dow Chemical Co., Thermal Laboratory, Midland, Mich.: $SiO_2(s)$, Dec 1962; $SiCl_4(g)$, $Al_2Cl_6(g)$, $AlCl_3(g)$, α-$Al_2O_3(s)$, March 1964.

(12) Crystalline complexes of $AlCl_3$ with a number of metal chlorides have been prepared: R. F. Belt and H. Scott, *Inorg. Chem.*, **3**, 1785 (1964); T. C. F. Munday and J. D. Corbett, *ibid.*, **5**, 1263 (1966). The crystal structure of $Co(AlCl_4)_2$ has been determined: J. A. Ibers, *Acta Cryst.*, **15**, 967 (1962).

Table II. Determination of $P_{Nd-Al-Cl}$ for the Complexation Reaction: $n_1NdCl_3(s) + n_2Al_2Cl_6(g) = Nd_{n_1}Al_{2n_2}Cl_{3n_1+6n_2}(g)$[a]

Experiment	T_{min}, °K	$10^3/T_{min}$, °K^{-1}	$\bar{T}$, °K	$P^0_{Al_2Cl_6}$	$P_{Al_2Cl_6}$	$A_{Nd-Al-Cl}$	$P_{Nd-Al-Cl} \times 10^3$
D							
$P^0_{Al_2Cl_6} = 2.469 \times 10^{-3}\bar{T}$ atm	778.6	1.2844	786	1.940	1.679	0.0490	8.712
$w_{NdCl_3} = 41.5 \times 10^{-3}$ g	658.0	1.5199	674	1.664	1.604	0.0210	3.202
$V = 74.12 \times 10^{-3}$ l.	858.5	1.1649	861	2.125	1.579	0.0747	14.55
$l = 19.30$ cm	605.3	1.6522	625	1.544	1.517	0.0133	1.880
$P_{Nd-Al-Cl} = (2.262 \times 10^{-4}\bar{T})A_{Nd-Al-Cl}$ atm							
E							
$P^0_{Al_2Cl_6} = 4.924 \times 10^{-3}\bar{T}$ atm	739.5	1.3524	750	3.691	3.425	0.1345	21.950
$w_{NdCl_3} = 57.3 \times 10^{-3}$ g	639.3	1.5643	656	3.232	3.157	0.0640	9.136
$V = 78.51 \times 10^{-3}$ l.	558.5	1.7907	583	2.868	2.850	0.0333	4.225
$l = 20.05$ cm	559.0	1.7891	583	2.871	2.850	0.0324	4.110
$P_{Nd-Al-Cl} = (2.176 \times 10^{-4}\bar{T})A_{Nd-Al-Cl}$ atm	592.7	1.6873	614	3.022	2.987	0.0427	5.705
F							
$P^0_{Al_2Cl_6} = 6.062 \times 10^{-3}\bar{T}$ atm	582.9	1.8909	556	*b*	*b*	0.015	1.802
$w_{NdCl_3} = 152 \times 10^{-3}$ g	579.4	1.7261	602	3.649	3.614	0.055	7.155
$V = 54.73 \times 10^{-3}$ l.	600.4	1.6657	621	3.765	3.715	0.069	9.260
$l = 20.2$ cm	672.6	1.4869	692	4.195	4.048	0.129	19.29
$P_{Nd-Al-Cl} = (2.161 \times 10^{-4}\bar{T})A_{Nd-Al-Cl}$ atm	667.1	1.4991	682	4.134	4.007	0.118	17.39
	703.7	1.4212	716	4.340	4.137	0.156	24.14
	782.7	1.2777	790	4.789	4.299	0.252	43.02
	781.6	1.2795	789	4.783	4.298	0.251	42.80
	862.6	1.1592	864	5.238	4.222	0.407	75.99
	981.7	1.0187	982	5.953	3.680	0.562	119.3
	1107.2	0.9032	1107	6.711	2.473	0.505	120.8
	1201.8	0.8321	1202	7.287	1.624	0.478	124.2
G							
$P^0_{Al_2Cl_6} = 9.813 \times 10^{-3}\bar{T}$ atm	522.1	1.9155	549	*b*	*b*	0.026	3.175
$w_{NdCl_3} = 43.4 \times 10^{-3}$ g	536.7	1.8634	563	*b*	*b*	0.041	5.134
$V = 73.83 \times 10^{-3}$ l.	549.2	1.8210	574	*b*	*b*	0.061	7.787
$l = 1962$ cm	561.5	1.7811	586	*b*	*b*	0.086	11.21
$P_{Nd-Al-Cl} = (2.224 \times 10^{-4}\bar{T})A_{Nd-Al-Cl}$ atm	570.5	1.7530	594	*b*	*b*	0.113	14.93
	577.0	1.7333	599	*b*	*b*	0.136	18.12
	583.8	1.7131	606	5.945	5.882	0.142	19.14
	603.3	1.6577	623	6.116	6.030	0.161	22.30
	656.5	1.5233	673	6.599	6.437	0.230	34.43
	669.9	1.4929	685	6.721	6.523	0.258	39.31
	719.7	1.3896	731	7.170	6.815	0.367	59.67
	761.8	1.3128	770	7.554	6.989	0.489	83.74
	778.1	1.2853	785	7.704	7.036	0.539	94.10
	809.8	1.2349	815	7.996	7.081	0.674	122.2

[a] See footnote *a* in Table I for definitions of symbols. [b] $AlCl_3$ present in liquid phase and the Al_2Cl_6 pressure is hence unknown.

Each listed value of absorbance for experiments B and C is the mean value of at least three separate runs with a temperature variation less than 0.5°. The limits of error in the absorbance readings are given as a ± value.

No consistent temperature variation was found, and the molar absorptivity of the gas species is considered to be independent of temperature. The mean value for each experiment is listed.

When compared at the same temperature, the pressures of Al_2Cl_6 vary for experiments A, B, and C in the ratio 1.0:4.9:9.5 with molar absorptivities in the ratio 17.0:18.5:19.0, respectively. One might ascribe the variations in molar absorptivities as due to a two-species equilibrium of the sort

$$NdAl_nCl_{3n+3}(g) + 0.5Al_2Cl_6(g) = NdAl_{n+1}Cl_{3n+6}(g) \quad \text{(IV)}$$

This explanation for the variation (but not the existence of reaction IV itself) is rejected for the following reasons.

In experiment A, one of the first to be performed, the cell was heated above 850°K. The resultant attack on the quartz windows and consequent loss of $NdCl_3$ may account for the fact that the molar absorptivity determined in experiment A is 10% less than for experiments B and C. However, the data are included for the sake of completeness. The molar absorptivities determined in experiments B and C are the same within experimental error, results being almost within the statistical variation of the absorbance readings.

The determination of the molar absorptivity of the complex is difficult because the total amounts of $NdCl_3$ used are 1-4 mg, and a slight degree of reaction with the quartz container or with small amounts of residual moisture could influence the results. The mean value for $\epsilon_{Nd-Al-Cl}$ derived from these measurements is

$$\bar{\epsilon}_{Nd-Al-Cl} = 18.8 \pm 0.4 \text{ l./(mole cm)}$$

over the pressure and temperature range studied. It is evident that an interpretation of the change in $\bar{\epsilon}_{Nd-Al-Cl}$ in terms of an equilibrium of type IV would be highly unreliable.

The assumption of a constant $\epsilon_{Nd-Al-Cl}$ independent of Al_2Cl_6 pressure leads to one of the following conclusions.

(a) Only one gaseous species is present; *i.e.*, equilibria of type IV are absent or occur only to a slight extent.

(b) If gaseous equilibria such as (IV) or more generally

$$\mathrm{Nd}_{n_1}\mathrm{Al}_{n_2}\mathrm{Cl}_{3n_1+3n_2}(\mathrm{g}) + n_3\mathrm{Al}_2\mathrm{Cl}_6(\mathrm{g}) = \mathrm{Nd}_{n_1}\mathrm{Al}_{n_2+2n_3}\mathrm{Cl}_{3n_1+3n_2+6n_3}(\mathrm{g}) \quad (\mathrm{V})$$

are of importance, then the molar absorptivities of the different gaseous Nd species are the same.

(c) If equilibria involving polynuclear species such as

$$\mathrm{Nd}_2\mathrm{Al}_4\mathrm{Cl}_{18}(\mathrm{g}) + \mathrm{Al}_2\mathrm{Cl}_6(\mathrm{g}) = 2\mathrm{NdAl}_3\mathrm{Cl}_{12}(\mathrm{g}) \quad (\mathrm{VI})$$

are of importance, then the "atom absorptivity" (molar absorptivity of species/number of Nd atoms in species) is the same for the different species.

Determination of Partial Pressures of $NdCl_3$–$AlCl_3$ Vapor Complexes. Reaction I was studied in four separate experiments with different pressures of $Al_2Cl_6(g)$, and the results are given in Table II. Chronologically, experiment F was run first in this series of experiments, and not enough time may have been allowed for equilibrium conditions to be established (filled points in Figure 1). In particular, short equilibration times were employed above 860°K because of rapid attack on cell windows.

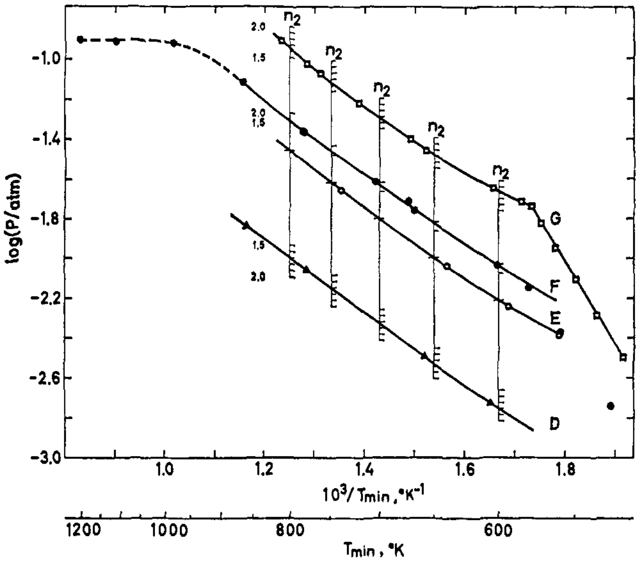

Figure 1. Experimental vapor pressure of Nd–Al–Cl complexes for equilibrium between $NdCl_3(s)$ and $Al_2Cl_6(g)$. Data for different experiments are given in Table II. The right side of eq 6 is plotted for 600, 650, 700, 750, and 800°K for evaluation of n_2 in the equilibrium: $n_1\mathrm{NdCl}_3(\mathrm{s}) + n_2\mathrm{Al}_2\mathrm{Cl}_6(\mathrm{g}) = \mathrm{Nd}_{n_1}\mathrm{Al}_{2n_2}\mathrm{Cl}_{3n_1+6n_2}(\mathrm{g})$.

An approximate calculation of the gas pressure using the van der Waals equation of state showed the pressure to differ from the ideal gas law pressure by less than 1%, and this correction was omitted. In Table II, $P^0_{\mathrm{Al_2Cl_6}}$ gives the pressure of $Al_2Cl_6(g)$ without correction for dissociation and reaction with $NdCl_3(s)$. $P_{\mathrm{Al_2Cl_6}}$ gives the actual pressure of Al_2Cl_6, taking into account equilibria I and III.

The equilibrium constant, K, for equilibrium III was calculated from values tabulated in JANAF Tables[11] for 400°K $\leq T \leq$ 1000°K. These values when fitted to the function

$$\log K_{\mathrm{III}} = A + (B/T) + (C/T^2) \quad (3a)$$

by the method of least squares give

$$\log K_{\mathrm{III}} = 6.649 - 5.684(10^3/T) - 1.607(10^5/T^2) \quad (3b)$$

The dimer pressure corrected for equilibrium III only is given by

$$P'_{\mathrm{Al_2Cl_6}} = 0.5[2P^0_{\mathrm{Al_2Cl_6}} + (K_{\mathrm{III}}/4) - \sqrt{P^0_{\mathrm{Al_2Cl_6}}K_{\mathrm{III}} + (K^2_{\mathrm{III}}/16)}] \quad (4)$$

$P_{\mathrm{Al_2Cl_6}}$ was obtained by correcting for consumption of Al_2Cl_6 due to equilibrium I using the calculated pressure of $\mathrm{Nd}_{n_1}\mathrm{Al}_{2n_2}\mathrm{Cl}_{3n_1+6n_2}$ with n_2 = 1.73 (see later). This correction was of minor importance (<3%).

The partial pressures of the Nd–Al–Cl complexes at the average cell temperatures $\bar{T}$ were calculated from eq 2 with $\epsilon_{\mathrm{Nd-Al-Cl}}$ = 18.8 l./(mole cm) at 17,030 cm^{-1}. Only mononuclear Nd complexes are assumed to be formed.

Values of log $P_{\mathrm{Nd-Al-Cl}}$ are plotted as function of $1/T_{\mathrm{min}}$ in Figure 1, assuming mononuclear Nd–Al–Cl complexes. Slightly curved lines are obtained. If polynuclear Nd complexes should be present, the $P_{\mathrm{Nd-Al-Cl}}$ in Figure 1 is then not the true pressure but the "atomic gas pressure" = (vapor pressure × number of Nd atoms in the species) which is independent of the number of Nd atoms in the species.

The reason for plotting $P_{\mathrm{Nd-Al-Cl}}$ *vs.* T_{min} rather than $\bar{T}$ is the following. Solid $NdCl_3$ originally in other parts of the cell is transported to the point of minimum temperature which was found to be in the center of the cell. Equilibrium I is established there. The partial pressure of the Nd–Al–Cl complexes, however, will be dependent on the temperature distribution throughout the cell. A reasonable way to take this fact into account is to use an average temperature to calculate the pressure. If a two-species gas equilibrium (equilibrium V) is of importance, the distribution of gaseous species will vary along the cell. However, such a situation would not influence the calculation of the partial pressure of Nd–Al–Cl complexes with the same number of Nd atoms and the same molar absorptivity.

For sample G, a break in the vapor pressure curve is observed at 577°K. Between this temperature and about 480°K, $NdCl_3$ dissolves in liquid $AlCl_3$ forming a homogenous phase. The strong variation of vapor pressure in this interval is due to changing content of $AlCl_3$ in the liquid phase thus changing the activity of $NdCl_3$. Since the primary object of the present investigation was to obtain information on Nd–Al–Cl complexes in the gas phase, vapor pressures of Nd–Al–Cl complexes above liquid $NdCl_3$–$AlCl_3$ mixtures were studied in detail only for experiment G. Using the data obtained for reaction with solid $NdCl_3$, vapor-pressure studies of the liquid mixtures will be useful for the determination of the activities in these mixtures and may form the subject of a later investigation.

The existence of the dissociation equilibrium III means that the vapor pressure of the complex reaches a maximum value at a certain temperature. Such a maximum is observed qualitatively for experiment F around 1000°K, but the equilibration time was too short to be certain that equilibrium values were reached in this temperature region.

Referring to the middle portions of the curves in Figure 1, the law of mass action for equilibrium I is given by the equation

$$P_{\mathrm{Nd}_{n_1}\mathrm{Al}_{2n_2}\mathrm{Cl}_{3n_1+6n_2}}/P^{n_2}_{\mathrm{Al_2Cl_6}} = K_{\mathrm{I}} \quad (5a)$$

or

$$\log P_{\mathrm{Nd}_{n_1}\mathrm{Al}_{2n_2}\mathrm{Cl}_{3n_1+6n_2}} = \log K_{\mathrm{I}} + n_2 \log P_{\mathrm{Al_2Cl_6}} \quad (5b)$$

The coefficient n_2 can be determined by performing two or more experiments with different pressures of Al_2Cl_6 at the same temperature. Thus, n_2 may be determined by comparing experiments D and E.

$$\log P(\mathrm{D})_{\mathrm{Nd}_{n_1}\mathrm{Al}_{2n_2}\mathrm{Cl}_{3n_1+6n_2}} = \log P(\mathrm{E})_{\mathrm{Nd}_{n_1}\mathrm{Al}_{2n_2}\mathrm{Cl}_{3n_1+6n_2}} + n_2(\log P(\mathrm{D})_{\mathrm{Al_2Cl_6}} - \log P(\mathrm{E})_{\mathrm{Al_2Cl_6}}) \quad (6)$$

In Figure 1, the right side of eq 6 is plotted for the temperatures 600, 650, 700, 750, and 800°K and n_2 = 1.5, 1.6, 1.7, 1.8, 1.9, and 2.0. Experiment E is chosen as the common reference. Similar plots are also shown for experiments F and G, still using E as reference.

In Table III are given the calculated values for n_2 with E as the reference. Corrected pressures of Al_2Cl_6 were utilized. It is to be remembered that uncertainties due to statistical variations are *ca.* three times as large for comparison of F–E than for D–E and G–E because of the smaller variation of Al_2Cl_6 pressure in going from experiment E to experiment F. Giving three times as much weight to the comparisons D–E and G–E than to F–E leads to a mean value for n_2 = 1.73. A small but significant decrease of n_2 with increasing temperature is observed, however. The numbers nearest to n_2 = 1.73 which give stoichiometric formulas for the gaseous species are 1.5 and 2, corresponding to the species $NdAl_3Cl_{12}$, $NdAl_4Cl_{15}$, or $Nd_2Al_4Cl_{18}$, respectively. Before proceeding with the discussion of the results, the data from experiments D, E, and F are presented in Figure 2 as log K_{VII} *vs.* $1/T$ for the imaginary reaction

Table III. Calculation of n_2 for Equilibrium I Choosing Experiment E as the Common Reference

	600°K	650°K	700°K	750°K	800°K
n_2 from expt D–E	1.80	1.75	1.72	1.70	1.68
n_2 from expt F–E	1.9	1.9	1.8	1.7	1.6
n_2 from expt G–E	1.83	1.73	1.68	1.65	1.65

$$\mathrm{NdCl_3(s)} + 1.73\mathrm{Al_2Cl_6(g)} \rightarrow \mathrm{Nd\text{-}Al\text{-}Cl(g)} \quad \mathrm{(VII)}$$

$$\log K_{\mathrm{VII}} = \log P_{\mathrm{Nd-Al-Cl}} - 1.73 \log P_{\mathrm{Al_2Cl_6}} \quad (7)$$

As expected, systematic deviations of log K_{VII} calculated from the different experiments are found. Thus, log K (experiment G)–log K (experiment D) is positive for 600°K and negative for 800°K. Furthermore, log K is not a linear function of $1/T$. A more nearly linear curve is obtained if the correction for the equilibrium $Al_2Cl_6(g) = 2AlCl_3(g)$ is omitted, but there is no reason to doubt the JANAF data[11] which are based on independent careful measurements by Fischer and Rahlfs,[13] Smits and Meijering,[14a] and Vrieland and Stull.[14b] Neglecting systematic deviations and fitting log K to the function

$$\log K_{\mathrm{VII}} = A + (B/T) + (C/T^2) \quad \mathrm{(8a)}$$

by the method of least squares gives

$$\log (K_{\mathrm{VII}}/(\mathrm{atm})^{-0.73}) = 1.923 - (4888/T) + (1148000/T^2) \quad \mathrm{(8b)}$$

The standard deviation $\sigma_{\log K_{\mathrm{VII}}}$ = 0.0197 which

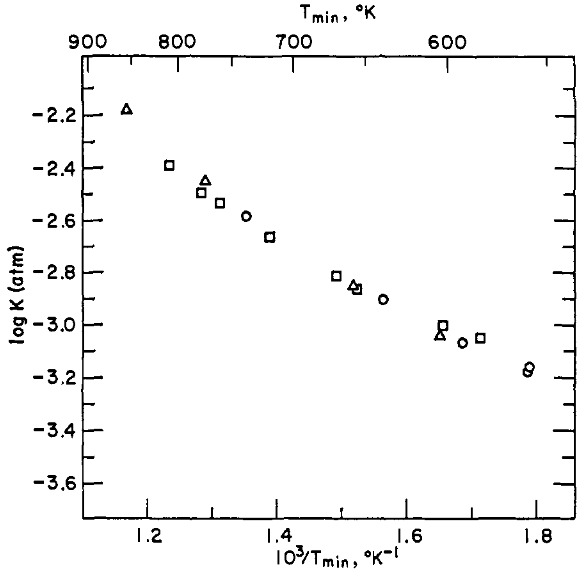

Figure 2. K_{VII} for the imaginary reaction $NdCl_3(s) + 1.73Al_2Cl_6(g) \rightarrow$ Nd-Al-Cl(g): D, △; E, ○; G, □.

corresponds to a per cent standard deviation in $\sigma_{P_{\mathrm{Nd-Al-Cl}}} = (10^{0.0197} - 1) \times 100 = 5\%$. Equation 8a should not be used outside the pressure and temperature range studied.

Stoichiometry of the Gaseous Nd–Al–Cl Species Based on Model Calculations of Vapor Pressure. The experimentally determined average coefficient $\bar{n}_2$ = 1.73 for equilibrium I can best be rationalized by considering an equilibrium involving two or more gaseous Nd–Al–Cl complexes.

The nonlinearity of log K_{VII} *vs.* $1/T$ and the decreasing value of n_2 (Figure 1) with increasing temperature indicate that the lower molecular weight species become more abundant at higher temperature.

Possible numbers and stoichiometries of gaseous species for values near n_2 = 1.73 are

$n_2 < 1.73$	$n_2 > 1.73$
n_2 = 1.5 $NdAl_3Cl_{12}$	n_2 = 2 $NdAl_4Cl_{15}$
n_2 = 1.5 $Nd_2Al_3Cl_{15}$	n_2 = 2 $Nd_2Al_4Cl_{18}$
n_2 = 1 $NdAl_2Cl_9$	n_2 = 2.5 $NdAl_5Cl_{18}$
n_2 = 1 $Nd_2Al_2Cl_{12}$	n_2 = 2.5 $Nd_2Al_5Cl_{21}$

Since equilibria between two species with the same number of Al atoms do not depend on $P_{\mathrm{Al_2Cl_6}}$, experiments in which the Al_2Cl_6 pressure is varied cannot be used to distinguish between the pair $NdAl_3Cl_{12}$ and $Nd_2Al_3Cl_{15}$ or the pair $NdAl_4Cl_{15}$ and $Nd_2Al_4Cl_{18}$. Without a mass spectrometric investigation, a choice between two such species could be made only if their spectra are sufficiently different or if the pressure of the pure solids were sufficiently high. In the absence of mass spectrometric data the probable assumption is made that only mononuclear species are present. Only two such equilibria will be considered

$$\mathrm{NdCl_3(s)} + m_1\mathrm{Al_2Cl_6(g)} = \mathrm{NdAl}_{2m_1}\mathrm{Cl}_{3+6m_1}\mathrm{(g)} \quad K_{\mathrm{VIII}} \quad \mathrm{(VIII)}$$

$$\mathrm{NdCl_3(s)} + m_2\mathrm{Al_2Cl_6(g)} = \mathrm{NdAl}_{2m_2}\mathrm{Cl}_{3+6m_2}\mathrm{(g)} \quad K_{\mathrm{IX}} \quad \mathrm{(IX)}$$

or (IX) – (VIII)

$$\mathrm{NdAl}_{2m_1}\mathrm{Cl}_{3+6m_1}\mathrm{(g)} + (m_2 - m_1)\mathrm{Al_2Cl_6(g)} = \mathrm{NdAl}_{2m_2}\mathrm{Cl}_{3+6m_2}\mathrm{(g)} \quad K_{\mathrm{X}} \quad \mathrm{(X)}$$

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(13) W. Fischer and O. Rahlfs, *Z. Anorg. Allgem. Chem.*, 205, 1 (1932).

(14) (a) A. Smits and J. L. Meijering, *Z. Physik. Chem.*, **B41**, 98 (1938); G. E. Vrieland and D. R. Stull, *J. Chem. Eng. Data*, 12, 532 (1967).

Table IV. Fit of Measured Vapor Pressure for Experiments D, E, and G to the Model Given by Eq 14

	A_1	B_1	A_2	B_2	% std dev for $P_{\text{Nd-Al-Cl}}$
$m_1 = 1.5$ $m_2 = 2$	0.547	−2353	−2.711	−370	2.4
$m_1 = 1.5$ $m_2 = 2.5$	0.089	−1920	−4.489	387	4.8
$m_1 = 1$ $m_2 = 2$	0.921	−2675	−1.646	−938	5.9
$m_1 = 1$ $m_2 = 2.5$	0.081	−1882	−2.362	−776	9.9

Table V. Calculated Entropies and Enthalpies of Reaction from $RT \ln K = T\Delta S - \Delta H$ Assuming ΔS and ΔH to be Constant over the Entire Temperature Range[a]

	All expt points included					Excluding meas for $P_{\text{Nd-Al-Cl}} = 0.122$ atm, 815°K				
Reaction	ΔS	$\sigma\Delta S$	ΔH	$\sigma\Delta H$	$\sigma P_{\text{Nd-Al-Cl}}$	ΔS	$\sigma\Delta S$	ΔH	$\sigma\Delta H$	$\sigma P_{\text{Nd-Al-Cl}}$
$NdCl_3(s) + 1.5Al_2Cl_6(g) = NdAl_3Cl_{12}(g)$	2.5	...	10.8	...	2.4%	2.3	0.3	10.6	0.3	2.1%
$NdCl_3(s) + 2Al_2Cl_6(g) = NdAl_4Cl_{15}(g)$	−12.4	...	1.7	...		−12.6	0.4	1.6	0.2	

[a] ΔS is given in eu and ΔH in kcal.

The pressure of the Nd–Al–Cl complex species is then given by

$$P_{\text{Nd-Al-Cl}} = K_{\text{VIII}}P^{m_1}{}_{Al_2Cl_6} + K_{\text{IX}}P^{m_2}{}_{Al_2Cl_6} \qquad (9)$$

The experimental data will now be tested using this model. The following procedure was adopted. Log K_{VIII} and log K_{IX} in eq 9 are required to be linear functions of $1/T$

$$\log K_{\text{VIII}} = A_1 + (B_1/T) \qquad (10)$$

$$\log K_{\text{IX}} = A_2 + (B_2/T) \qquad (11)$$

Equation 9 can then be rewritten

$$P_{\text{Nd-Al-Cl}} = \exp\{A_1 + (B_1/T)\}(P_{Al_2Cl_6})^{m_1} + \exp\{A_2 + (B_2/T)\}(P_{Al_2Cl_6})^{m_2} \qquad (12)$$

Equation 12 was employed for determining least-squares values for A_1, B_1, A_2, and B_2 utilizing the experimental values for experiments D, E, and G. In order not to give undue statistical weight to experiments at high vapor pressures, a least-squares per cent sum F was minimized.

$$F = \sum \left(\frac{P_{\text{Nd-Al-Cl}}(\text{exptl}) - P_{\text{Nd-Al-Cl}}(\text{calcd})}{P_{\text{Nd-Al-Cl}}(\text{exptl})} \times 100\right)^2 \qquad (13)$$

$P_{Al_2Cl_6}$ was calculated as a function of T using eq 3b and 4 and correcting for consumption of Al_2Cl_6. Since $P_{\text{Nd-Al-Cl}}(\text{calcd})$ is a nonlinear function of A_1, B_1, A_2, and B_2, a general program for fitting a nonlinear model to experimental data developed by Hertzberg[15] based on an algorithm by Nelder and Mead[16] has been utilized. It is an iteration method using the following strategy. Starting values for the n variables are chosen. The function is minimized by comparing the function values at $n + 1$ vertices of a general simplex. New simplexes are continually formed by reflecting the vertex giving the highest value in the hyperplane of the remaining points. The simplex adapts itself to the local landscape and goes down to the final minimum. The results are given in Table IV. Excellent agreement is found for $m_1 = 1.5$, $m_2 = 2$, corresponding to the species $NdAl_3Cl_{12}$ and $NdAl_4Cl_{15}$. These species are the most probable ones since they bracket the observed average stoichiometry: $NdAl_{3.46}Cl_{13.38}$. The two-species model corresponds to the following simultaneous equilibria.

$$NdCl_3(s) + 1.5Al_2Cl_6(g) = NdAl_3Cl_{12}(g) \qquad (XI)$$

$$NdCl_3(s) + 2Al_2Cl_6(g) = NdAl_4Cl_{15}(g) \qquad (XII)$$

$$(XII) - (XI):\quad NdAl_3Cl_{12}(g) + 0.5Al_2Cl_6(g) = NdAl_4Cl_{15}(g) \qquad (XIII)$$

The standard deviation of $P_{\text{Nd-Al-Cl}}$ is only 2.4%. The variance ratio: next best model ($m_1 = 1.5$, $m_2 = 2.5$)/best model ($m_1 = 1.5$, $m_2 = 2$) = 4.0.

According to Fischers F test,[17] assuming a normal distribution with 13 degrees of freedom, a variance ratio of 4.1 is needed to make the probability that the models belong to the same normal population <1%. It is, hence, concluded that the model with $m_1 = 1.5$, $m_2 = 2$ is significantly better than the others. This model is further supported by the observation that the deviations show no systematic behavior, which is not the case for the other models.

Accepting the model with $m_1 = 1.5$ and $m_2 = 2$, the vapor pressure of Nd–Al–Cl is hence given by

$$P_{\text{Nd-Al-Cl}} = \exp\{0.547 - (2353/T)\}(P_{Al_2Cl_6})^{1.5} + \exp\{-2.711 - (370/T)\}(P_{Al_2Cl_6})^2 \qquad (14)$$

Using the equation

$$\log K = \frac{\Delta S°}{R \ln 10} - \frac{\Delta H°}{RT \ln 10} \qquad (15)$$

the thermodynamic functions are calculated and given in Table V.

The least-squares per cent sum F which was minimized with respect to entropies and enthalpies of reaction has the property that the minimum is flat. As a consequence, mutual and balancing changes in the entropies and enthalpies of reaction around the minimum result in small changes in $P_{\text{Nd-Al-Cl}}(\text{calcd})$. Thus, the computer program was not able to give the standard deviations of the thermodynamic quantities.

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(15) T. Hertzberg, to be submitted for publication.

(16) J. A. Nelder and R. Mead, *Computer J.*, 7, 308 (1965).

(17) M. G. Kendall and A. Stuart, "The Advanced Theory of Statistics," Vol. 1, C. Griffin and Co., London, 1958, p 407.

Table VI. Spectral Characteristics of Nd-Al-Cl Gas Complexes in Equilibrium with Gaseous Al_2Cl_6 and Solid $NdCl_3$ at $P_{Al_2Cl_6}$ = 6.99 Atm and 762°K

Absorption max, $cm^{-1} \times 10^{-3}$	11.34	12.39	13.32	14.60	15.20	17.01	18.92	19.42	21.05	23.09	24.16	27.89	28.30	30.08
Molar absorptivity above background curve, l./(mole cm)	1.4	3.6	3.1	0.3	0.3	18.8	3.0	1.3	0.6	0.4	0.2	2.1	2.4	0.4

However, if one ignores the experimental point showing the largest deviation (T_{min} 809.8°K, $P_{Nd-Al-Cl}$ 0.122 atm), the average standard deviation of the entropy of reaction is 0.35 eu and the average standard deviation of the enthalpy of reaction is 0.25 kcal. The corresponding relative standard deviation of $P_{Nd-Al-Cl}$ decreases from 2.4 to 2.1%.

Allowing for the neglect of the point with the largest standard deviation and nonstatistical errors, a realistic estimate of standard deviations of the entropies and enthalpies of reaction are considered to be 1 eu and 1 kcal, respectively.

In order to demonstrate the increase in volatility of $NdCl_3(s)$ due to complexation, one can calculate the volatility ratio: $V_r = P_{Nd-Al-Cl}$ (1 atm of $Al_2Cl_6)/P_{NdCl_3}$ (inert atmosphere). Using the vapor pressure data of Shimazaki and Niwa[8] and $P_{Nd-Al-Cl}$ calculated from eq 14

$$V_r = \frac{8.92 \times 10^{-4}}{7.78 \times 10^{-17}} = 1.15 \times 10^{13} \text{ at } 600°\text{K}$$

$$V_r = \frac{4.71 \times 10^{-3}}{1.59 \times 10^{-10}} = 2.96 \times 10^{7} \text{ at } 800°\text{K}$$

The apparent vapor pressure of $NdCl_3$ in 1 atm of Al_2Cl_6 is increased by a factor of 10^{13} and 3×10^7 at 600 and 800°K, respectively.

As already mentioned, the experimental data do not completely exclude from consideration gaseous species with two Nd atoms or models involving more than two species. However, equilibria involving only $NdAl_3Cl_{12}$ and $NdAl_4Cl_{15}$ are in accordance with experimentally determined stoichiometries, with the observation that the lighter species becomes more abundant at higher temperatures and with log K's which are linear functions of $1/T$. The spectra of the two species are found to have the same molar absorptivity: 18.8 l./(mole cm) at ν 17,030 cm^{-1}. This is in sharp contrast to observed changes in the molar absorptivity for the same transition[9] in going from $NdI_3(g)$ (ν 16,334 cm^{-1}, ϵ 345, T 1360°K) to $NdBr_3(g)$ (ν 16,469 cm^{-1}, ϵ 116, T 1468°K). Hence, for the two Nd-Al-Cl species, similar surroundings around the Nd^{3+} ion are indicated. Structural formulas consistent with these facts are $Nd(AlCl_4)_3$ and $Nd(AlCl_4)_2(Al_2Cl_7)$ or $NdCl(AlCl_4)(Al_2Cl_7)$ and $NdCl(Al_2Cl_7)_2$. Structures with different numbers of chloride ions directly bonded to the Nd ion would not be as likely to be in accord with the spectral similarity of the species.

An approximate calculation of the entropy of equilibrium XI was made, assuming the complex $Nd(AlCl_4)_3$. The entropy calculated from statistical thermodynamics is in agreement with the observed entropy: 2.5 eu. The calculation is not considered conclusive, however, since the small entropy of reaction is the difference between the large entropy of $Nd(AlCl_4)_3$ and that of the reactants.

The increase in molar absorptivity from $NdBr_3(g)$ to $NdI_3(g)$ was considered to be due to increased covalency.[9] The lower molar absorptivity of the aluminum chloride complexes indicates a low degree of covalency and points to primarily ionic interactions of Nd^{3+} with $AlCl_4^-$ and $Al_2Cl_7^-$.

Spectrum of the Nd-Al-Cl Complexes. In Figure 3 is shown a typical absorption spectrum for the gaseous species above solid $NdCl_3$ for sample G at 762°K. This particular experiment was chosen since the gas pressure of the complex was sufficiently high to reveal absorption maxima down to a molar absorptivity of 0.2 l./(mole cm). Background scattering has been included, but a tentative background curve is given. Table VI lists the molar absorptivities of absorption maxima, setting the molar absorptivity of the peak at 17,030 cm^{-1} = 18.8 l./(mole cm). All recorded spectra were examined for changes of absorption maxima and molar absorptivity with temperature and pressure. As discussed earlier, no change in location and molar absorptivity for the absorption maxima at 17,030 cm^{-1} was found. For all absorption maxima no significant change of the location of the absorption maxima could be detected larger than ±20 cm^{-1}. For the same sample a slight decrease of molar absorptivity with increasing temperature was observed, the temperature variation for the two next strongest absorption peaks at 12,400 and 13,300 cm^{-1} being about −0.15%/°K giving a decrease in molar absorptivity of 0.5 l./(mole cm) over 100°K. The peaks at 12,400 and 13,300 cm^{-1} were examined for changes in molar absorptivity at constant temperature and changing pressure. No change was observed within the experimental uncertainty, ±0.2 l./mole with the pressure variation (1:6) investigated.

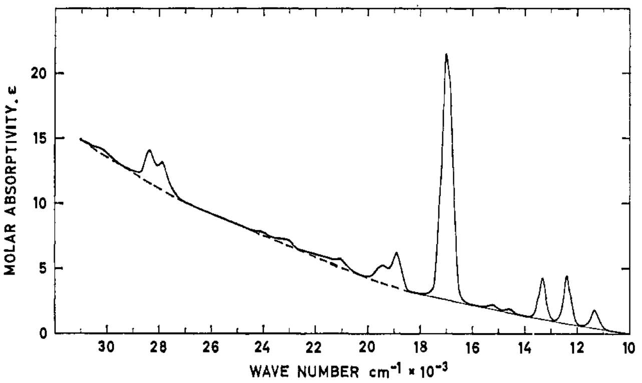

Figure 3. Absorption spectrum of Nd-Al-Cl gas complexes for equilibrium between solid $NdCl_3$ and gaseous $AlCl_3$ at 6.99 atm of Al_2Cl_6 and 762°K. A tentative background curve is given.

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Preferential Solvation and the Mechanisms of Thermal and Photochemical Solvolysis of the Hexathiocyanatochromate(III) Ion in Acetonitrile–Water Mixtures[1]

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Abstract: The nmr method for determining the composition of the solvation shell of a paramagnetic solute introduced by Frankel, Stengle, and Langford has been applied to reveal the strong preference of $Cr(NCS)_4{}^{3-}$ for CH_3CN in $CH_3CN–H_2O$ mixtures. The rate of loss of the first SCN^- from this complex has been measured as a function of solvent-shell composition. The thermal solvolysis reaction rate decreases linearly with the fraction of water (the reactive solvent) in the solvation shell revealing the requirement for one water molecule as a stoichiometric component of the transition state. Solvolysis by D_2O, methanol, and pyridine proceeds at nearly the same rate as hydrolysis. The corresponding photolysis is nearly independent of solvent-shell composition. A dissociative interchange mechanism for thermal solvolysis would explain these results. The photoexcited state is expected to have a lifetime sufficiently long to allow rearrangement of the solvation shell after "activation."

Any second or higher order solution reaction which proceeds at a rate significantly less than the diffusion control limit may be considered as requiring at least two elementary steps. For example, the solvolytic reaction of a transition metal complex would be

$$\mathrm{MX} + \mathrm{S} \rightleftarrows \mathrm{E} \qquad (1)$$

$$\mathrm{E} \longrightarrow \mathrm{MS} + \mathrm{X}$$

where MX is some substrate complex, S is the reactive solvent species, E is the *encounter*[3] complex, and MS and X are the products. The formation and dissociation of an encounter complex must, under normal circumstances, proceed at a rate approximating diffusional control.[4] Thus, the slow step leading to products does not significantly perturb the equilibrium of the encounter step. If the equilibrium for the encounter may be studied independently, correlation of the reaction rate with the population of encounter complexes between MX and S may reveal the number of solvent molecules, S, required as stoichiometric components of the transition state for product formation.

In a pure solvent, the encounter complex population is clearly invariant, which is the *fundamental* reason for pseudo-first-order kinetics. In a mixed solvent (one "unreactive" component) the population will vary according to the preference of the solute for solvation by one or the other component. In the event that there is a *strong* preference for one solvent component, it may be that the probability of encounter with the reactive component varies significantly without a correspondingly large change in the relevant parameters for the bulk of the solvent (*e.g.*, dielectric constant). Just such a situation seems to arise with respect to solutions of $K_3[Cr(NCS)_6]$ in acetonitrile–water mixtures.[5]

The strong preference in this case is that of $Cr(NCS)_6{}^{3-}$ for acetonitrile and the reactive solvent is water. The preferential solvation information is derived from studies of the effect of the paramagnetic solute on the nmr relaxation times of protons of the solvent molecules. This method, recently suggested,[5,6] merits brief recapitulation.

The transverse relaxation time, T_2, of the protons on a solvent-molecule will be greatly reduced by a paramagnetic solute. In cases of solvation in the outer coordination sphere, this effect depends upon dipolar coupling between the paramagnetic electrons and the protons which enters the relaxation equations with an inverse sixth power distance dependence.[7] As a result, it is a good approximation to partition the solution into a paramagnetic environment (the solvation shell) and a diamagnetic environment (the bulk solvent). When exchange between these two environments is

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[1] We acknowledge support from the National Research Council (Canada) and the Air Force Office of Scientific Research.

[2] To whom correspondence should be addressed at Carleton University; Alfred P. Sloan Fellow, 1968–1970.

[3] A pair of partners trapped in the "solvent cage."

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