ESTIMATION OF VAPOUR PRESSURES OF NEODYMIUM TRICHLORIDE HYDRATES

RONALD J. ROY * and GEORGES J. KIPOUROS

Department of Mining and Metallurgical Engineering, Technical University of Nova Scotia, P.O. Box 1000, Halifax, Nova Scotia B3J 2X4 (Canada)

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ABSTRACT

A thermodynamic prediction of the vapour pressures of neodymium trichloride hydrates is attempted. The thermodynamic treatment is based on estimated as well as measured data. Specific heats and entropies of the various neodymium trichloride hydrates were estimated by analogy to the magnesium chloride-hydrates system. Heats of formation of the lower hydrates could only be approximated by their similarity with the corresponding magnesium chloride and praseodymium chloride systems. Vapour pressures over the various hydrates were then estimated and compared with the published values. Various proposed dehydration schemes are discussed.

INTRODUCTION

Recent trends show that the commercial consumption of the rare earths is expanding rapidly due to the role of neodymium metal, which is now being used in aluminium alloys, catalysts, capacitors, electronics and permanent magnets [1]. Future prospects for neodymium depend on the success of Nd-based permanent magnets [2–5]. To reduce the cost of neodymium production, new thermite and electrolytic methods have been proposed [6–8] using $NdCl_3$ as a feed material. The preparation of anhydrous neodymium trichloride may then be the critical factor for the success of these processes.

The dehydration of neodymium trichloride hexahydrate ($NdCl_3 \cdot 6H_2O$) to produce anhydrous neodymium trichloride ($NdCl_3$) is an essential step in the recovery of neodymium metal by fused salt electrolysis. Depending on the required purity of the cell feed, the drying may be conducted in the absence or presence of hydrogen chloride. Unavoidably some hydrolysis products such as $NdOCl$ or $Nd(OH)_2Cl$ may form.

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* Present address: Noranda Minerals, Matagami Division, Matagami, Quebec, J0Y 2A0, Canada.

TABLE 1

Dehydration reactions

Reaction		Scheme			Reference		
1	$NdCl_3 \cdot 6H_2O \rightarrow NdCl_3 \cdot 5H_2O + H_2O$	I			9		
2	$NdCl_3 \cdot 6H_2O \rightarrow NdCl_3 \cdot 4H_2O + 2H_2O$		II			15	
3	$NdCl_3 \cdot 6H_2O \rightarrow NdCl_3 \cdot 3H_2O + 3H_2O$			III			12, 13
4	$NdCl_3 \cdot 5H_2O \rightarrow NdCl_3 \cdot 4H_2O + H_2O$	I			9		
5	$NdCl_3 \cdot 4H_2O \rightarrow NdCl_3 \cdot 3H_2O + H_2O$		II			15	
6	$NdCl_3 \cdot 4H_2O \rightarrow NdCl_3 \cdot H_2O + 3H_2O$	I			9		
7	$NdCl_3 \cdot 3H_2O \rightarrow NdCl_3 \cdot 2H_2O + H_2O$		II	III		15	12, 13
8	$NdCl_3 \cdot 2H_2O \rightarrow NdCl_3 \cdot H_2O + H_2O$		II	III		15	12, 13
9	$NdCl_3 \cdot H_2O \rightarrow NdCl_3 + H_2O$	I	II	III	9	15	12, 13

The mechanism of the dehydration process has recently been investigated by differential thermal analysis and X-ray powder diffraction. The investigation of the intermediates [9] revealed the formation of hydroxychloride during the dehydration. Differential thermal analysis was first used for identification purposes [10], while subsequent investigations [11–15] have proposed various dehydration schemes mainly on the basis of the observed weight losses. Table 1 outlines the dehydration reactions proposed by various investigators. Some vapour pressure measurements have been reported [13–15,16] and one of the hydrolysis reactions has been investigated to some extent [17].

The fact that three different schemes have been proposed to explain the dehydration is a clear indication of the controversy regarding the mechanism. The difficulty arises from the complexity of the system and the limitations of the analytical techniques to isolate and identify the intermediate hydrates. For the same reason, very few thermodynamic data are available for the $NdCl_3–H_2O$ system.

Possible reactions which may prevent the formation of pure, anhydrous $NdCl_3$ from the dehydration of $NdCl_3 \cdot 6H_2O$ have been identified [9,17]. Any hydrolysis taking place is probably caused by water evolving during the dehydration and may be described by

$$NdCl_3 + H_2O \rightarrow NdOCl + 2HCl \tag{1}$$

In the presence of oxygen during the dehydration [9] hydrolysis by reaction (1) may be accompanied by the reaction

$$NdCl_3 + 1/2\ O_2 \rightarrow NdOCl + Cl_2 \tag{2}$$

The formation of neodymium hydroxychloride, $Nd(OH)_2Cl$, during dehydration [9] has been observed and it was attributed to the following reaction

$$NdCl_3 + 2H_2O \rightarrow Nd(OH)_2Cl + 2HCl \tag{3}$$
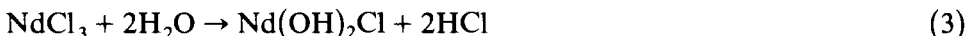
As the dehydration proceeds to higher temperatures, the neodymium hydroxychloride formed by reaction (3) decomposes to NdOCl according to the reaction

$$Nd(OH)_2Cl \rightarrow NdOCl + H_2O \tag{4}$$

It is possible to prevent the above reactions from taking place by maintaining the proper pressure of HCl or by keeping the ratio of the vapour pressures of water and hydrogen chloride at a proper value which is defined by the equilibrium conditions of reaction (3). Accurate experimental or predicted vapour pressure data are required.

The present investigation was undertaken in order to estimate thermodynamic data for all of the hydrates. Based on these data, energy requirements for each of the proposed dehydration and hydrolysis reactions are calculated and the equilibrium water vapour pressures over the various hydrates are derived. These equilibrium water vapour pressures are then compared with published [13,14] values in an attempt to elucidate the dehydration scheme. Methods of avoiding contamination of the product, $NdCl_3$, with NdOCl are also discussed.

THEORY

Methods for deriving equilibrium relationships from reaction energy requirements in the form of Σ-functions have been adequately discussed in textbooks [18,19]

For a chemical reaction,

$$A + B = C + D$$
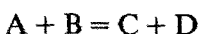
the temperature variation of the standard heat of reaction, $\Delta H^{\ominus}$, may be expressed as

$$\Delta H^{\ominus} = \Delta H_0 + aT + (b/2)T^2 - cT^{-1} \tag{5}$$

where ΔH_0 is a constant of integration and can be evaluated if the standard heat of reaction is known at a specific temperature. The coefficients a, b and c express the temperature variation of the heat capacities of the reaction

$$\Delta C_p = C_{p,C} + C_{p,D} - C_{p,A} - C_{p,B} = a + bT - cT^{-2} \tag{6}$$

where $a = a_C + a_D - a_A - a_B$, etc. The constants a_i, b_i and c_i are empirically determined from the specific heats over the temperature range of interest.

The Gibbs–Helmholtz equation,

$$\Delta G^{\ominus}/T = - \int (\Delta H^{\ominus}/T^2) \, dT \tag{7}$$

may be used to determine $\Delta G^{\ominus}$, the standard free energy of the reaction as a function of temperature. By substituting eqn. (6) into eqn. (7) an expression is obtained for the standard free energy of reaction

$$\Delta^{\ominus} G^0 = \Delta H_0 - aT \ln T - (b/2)T^2 + (c/2)T^{-1} + IT \tag{8}$$

where I is another integration constant.

The fundamental equation, $\Delta G^{\ominus} = \Delta H^{\ominus} - T \Delta S^{\ominus}$, relates the standard entropy of reaction with the standard heat and free energy of reaction

$$\Delta S^{\ominus} = a + a \ln T + (b/2)T - cT^{-2} - I \tag{9}$$

If standard entropy values for both products and reactants are known at a particular temperature, then the standard entropy of reaction, $\Delta S^{\ominus} = S_C^0 + S_D^0 - S_A^0 - S_B^0$, can be evaluated at that temperature. This, in turn, may be used in combination with eqn. (9) to determine the integration constant I.

With known values for both ΔH_0 and I, the energy requirements of the reactions can be calculated over the temperature range of interest via eqn. (8). The standard free energy of reaction can also be expressed in terms of the equilibrium constant, K, of the reaction

$$\Delta G^{\ominus} = -RT \ln K \tag{10}$$

The equilibrium constant involves the vapour pressure of the gaseous species participating in the reaction and the activities of the condensed phases. In this work the latter will be assumed to be at unit activity which implies that there is no solid solubility amongst the various hydrates.

PROCEDURE

Application of eqns. (5)–(10) requires the availability of the basic thermo-dynamic data for all compounds. Heat capacities, standard entropies and standard heats of formation are required for all products and reactants of the reactions under consideration.

Only limited thermodynamic data for $NdCl_3$ and its hydrates have been published as shown in Table 2, which indicates that there are no data available for the intermediate hydrates of $NdCl_3$, only low temperature heat capacities are available for $NdCl_3$ and $NdCl_3 \cdot 6H_2O$ and there is no value for the standard entropy for $NdCl_3$. All these data have to be estimated before an estimation of the vapour pressure can be attempted. Thermody-namic data available for the oxysalts in reactions (1)–(4) are also limited and consequently they have to be estimated.

The problem of insufficient thermodynamic data for equilibrium calcula-tions is common. Methods have been devised to estimate unknown data and have been described in textbooks [19,27].

TABLE 2

Published data for compounds relevant to $NdCl_3 \cdot 6H_2O$ dehydration

Property	$NdCl_3$	$NdCl_3 \cdot 6H_2O$	NdOCl	$Nd(OH)_2Cl$
Heat of formation (cal mol^{-1})	-250000 [20] -248996 [22] -245620 [24]	-687000 [21] -683580 [23]		
Heat of dissociation (cal mol^{-1})	-166491 [25]			
Heat of solution (cal mol^{-1})	-37489 [26]	-9103 [27]	-28.6 [28]	-19.9 [28]
Standard entropy (cal mol^{-1} K^{-1})		99.7 [21] 99.4 [27]	22.6 [19]	26.8 [9]
Heat capacity	Specific heats measured at temperatures below 350 K [26]			

In the present work since low temperature heat capacity data exist for both $NdCl_3$ and $NdCl_3 \cdot 6H_2O$, heat capacities of the form $C_p = a + bT$ were extrapolated [29] over the temperature range of interest. Figure 1 demonstrates the extrapolation of low temperature heat capacity data for the two compounds. Heat capacities for intermediate hydrates were estimated from these low temperature data, based on trends apparent in similar hydrate systems. More specifically, it has been observed [29] that the a and b coefficients in the heat capacities of $MgCl_2$ intermediate hydrates are linear progressive functions of the number of moles of the crystallization water. This linear progression of a and b coefficients with moles of water of crystallization is also assumed valid for $NdCl_3$ and its hydrate compounds. The heat capacity of a solid is mostly due to the excitation of vibrational degrees of freedom in three dimensions [27]. With each additional mole of
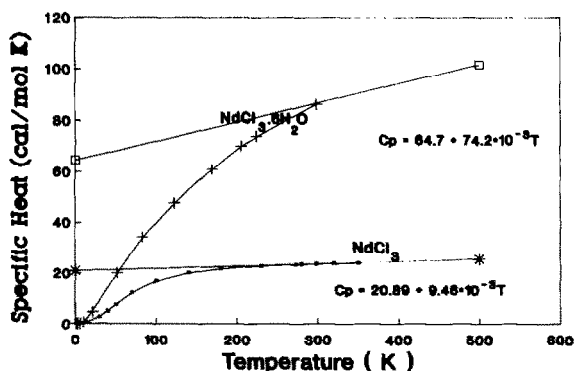
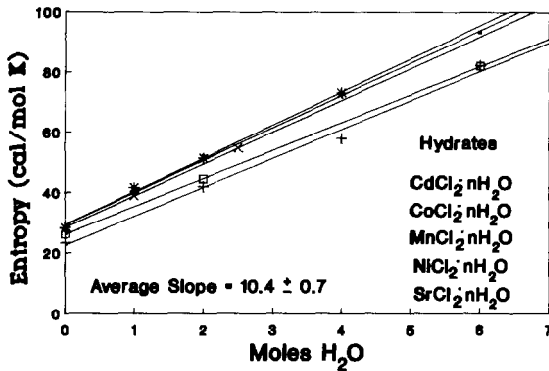Fig. 1. Specific heat versus temperature for $NdCl_3$ and $NdCl_3 \cdot 6H_2O$.

Fig. 2. Standard entropy versus moles water of crystallization for various chloride hydrates.

H₂O, the capacity of the hydrate to vibrate in three dimensions is increased by a uniform amount.

Therefore, the temperature dependence of C_p for intermediate hydrates can be interpolated from the heat capacities of $NdCl_3$ and $NdCl_3 \cdot 6H_2O$ according to,

$$a_n = 20.89 + 7.3n \tag{11}$$

$$b_n = (9.46 + 10.79n) \times 10^{-3} \tag{12}$$

where n is the number of moles of H_2O of crystallization.

The standard entropy of $NdCl_3$, $S^{\ominus}_{NdCl_3}$, was estimated from published [17] data of the standard entropy of reaction (1) as 32.8 e.u. Latimer's method [30] was then used to confirm this estimate (31.9 e.u.). From this value and that of $NdCl_3 \cdot 6H_2O$, standard entropies were estimated for the intermediate hydrates, using an approach similar to that used for heat capacities. As shown in Fig. 2 the standard entropy values of intermediate hydrates for a number of chloride hydrate systems are linear progressive functions of the number of moles of water of crystallization. For the hydrates shown in Fig. 2, there was an average increase of 10.4 e.u. for each additional mole of H_2O as compared to the recommended [27] value of 9.4 e.u. It is recognized that there is a difference in valence between the cations included in the hydrates in Fig. 2 and Nd^{3+}. However, this difference is accounted for in the standard entropies of the anhydrous salts. Therefore, the linear progression of standard entropy with the number of moles of crystallization water was assumed valid for $NdCl_3$ and its hydrates. The standard entropies for intermediate hydrates can then be interpolated from data available for $NdCl_3$ and $NdCl_3 \cdot 6H_2O$ as,

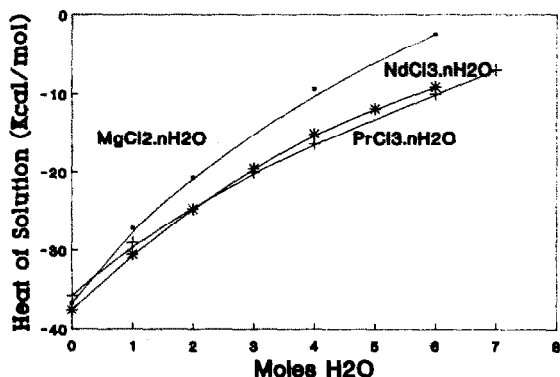$$S^{\ominus}_{NdCl_3 \cdot nH_2O} = 32.8 + 11.1 \times n \text{ e.u.} \tag{13}$$

Fig. 3. $\Delta H_{\text{solution}}$ versus moles water of crystallization for MgCl$_2$, PrCl$_3$ and NdCl$_3$ hydrates.

where n is the number of moles of crystallization water in the hydrate. An increase of 11.1 e.u. for each additional mole of H$_2$O is within the average increase for the hydrates shown in Fig. 2; 10.4 ± 0.7 e.u.

Estimation of standard heats of formation, $\Delta H_{298}^{\ominus}$, for the intermediate hydrates requires accurate experimental values of the heats of solution of the hydrates. The latter can be estimated only by analogy with similar compounds and systems. There is no linear progressive relation to the moles of crystallization water due to the strong solvent–solute interactions and dilution effects. Figure 3 shows the variation of the experimental heats of solution for hydrates of MgCl$_2$ [29] and PrCl$_3$ [31,32] as a function of number of moles of water of crystallization. An estimated curve for the NdCl$_3$ hydrates has been derived and is also included in Fig. 3.

Standard heats of formation for the intermediate hydrates were then calculated from these estimated heats of solution and reported values of the heat of dissociation according to the following thermodynamic cycle:

Reaction			ΔH_{298} (cal mol^{-1})
(a)	Nd + 3H$^+$	→ Nd^{3+} + 3/2H$_2$	−166491 [24]
(b)	NdCl$_3 \cdot n$H$_2$O	→ Nd^{3+} + 3Cl$^-$ + nH$_2$O	Fig. 3
(c)	3/2H$_2$ + 3/2Cl$_2$	→ 3H$^+$ + 3Cl$^-$	−117690 [33]
(d)	nH$_2$ + n/2O$_2$	→ nH$_2$O	−68318n [29]

Summation of the above equations yields the standard heat of formation of the corresponding hydrate from its elements

(e) Nd + 3/2Cl$_2$ + nH$_2$ + n/2O$_2$ → NdCl$_3 \cdot n$H$_2$O ΔH_e
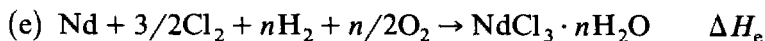
The estimated standard heats of formation at 298 K are given in Table 3 along with all the other thermodynamic data estimated in this work. The published standard free energy relationship [17] for reaction (1) was used to determine the equilibrium vapour pressures of H$_2$O and HCl required to avoid hydrolysis. The ΔC_p implicit in this relationship is that estimated [17]

TABLE 3

Estimated thermodynamic data for $NdCl_3$ and its hydrates

Compound	$C_p = a + bT$ (cal mol^{-1} K^{-1})		Standard entropy	Standard heat of formation
	a	b ($\times 10^{-3}$)	(cal mol^{-1} K^{-1})	
				(kcal mol^{-1})
$NdCl_3$	20.89	9.46	32.8	-246.7
$NdCl_3 \cdot H_2O$	28.19	20.25	43.9	-322.0
$NdCl_3 \cdot 2H_2O$	35.49	31.04	55.0	-396.1
$NdCl_3 \cdot 3H_2O$	42.8	41.83	66.1	-469.6
$NdCl_3 \cdot 4H_2O$	50.1	52.62	77.2	-542.4
$NdCl_3 \cdot 5H_2O$	57.4	63.41	88.3	-613.9
$NdCl_3 \cdot 6H_2O$	64.7	74.2	99.4	-685.0

for the hydrolysis of lanthanum trichloride, $LaCl_3$. However, the agreement between the calculated free energies and values determined experimentally is relatively good [17].

Analysis of reactions involving $Nd(OH)_2Cl$ was not conducted in the present work due to insufficient data. Heat capacity data are not available for $Nd(OH)_2Cl$ and would be difficult to estimate. As the lowest transition temperature for $Nd(OH)_2Cl$ is unknown, the temperature dependence of its heat capacity cannot be estimated using the method described previously.

RESULTS AND DISCUSSION

Dehydration reactions

Reaction energy requirements and equilibrium water vapour pressures were calculated according to eqns. (5)–(10) for all of the proposed dehydration reactions in Schemes I–III of Table 1. Data for these calculations are taken from Tables 2 and 3 for the neodymium compounds and from standard thermodynamic compilations [19] for H_2O. Vapour pressures are calculated [29,34] by substituting for the equilibrium constant in eqn. (10) and assuming that all solids are at unit activity, i.e. there is no solid solubility between the hydrates or between the hydrates and the products of hydrolysis. The results of these calculations are shown in Table 4. In an attempt to elucidate the reaction scheme, estimated and experimentally determined data are compared in a step-by-step dehydration approach.

First dehydration step

As shown in Table 1, three different reactions have been proposed for the first dehydration step. Estimated and published [14,15] equilibrium water

TABLE 4

Vapour pressure equations for the dehydration and hydrolysis reactions of $NdCl_3 \cdot 6H_2O$

Reactions	$Log\ P = A + B \times 10^{-4}\ T + C\ \log T + D\ T^{-1} + E\ T^2$				
	A	B	C	D	E
Dehydration reactions					
$NdCl_3 \cdot 6H_2O_{(2)} = NdCl_3 \cdot 5H_2O_{(s)} + H_2O_{(g)}$	7.97653	−9.27	−0.00503	−2977.2	
$NdCl_3 \cdot 6H_2O_{(s)} = NdCl_3 \cdot 4H_2O_{(s)} + 2H_2O_{(g)}$	7.97653	−9.27	−0.00503	−3031.07	
$NdCl_3 \cdot 6H_2O_{(s)} = NdCl_3 \cdot 3H_2O_{(s)} + 3H_2O_{(g)}$	7.97653	−9.27	−0.00503	−3138.65	
$NdCl_3 \cdot 5H_2O_{(s)} = NdCl_3 \cdot 4H_2O_{(s)} + H_2O_{(g)}$	7.97653	−9.27	−0.00503	−3084.95	
$NdCl_3 \cdot 4H_2O_{(s)} = NdCl_3 \cdot 3H_2O_{(s)} + H_2O_{(g)}$	7.97653	−9.27	−0.00503	−3353.79	
$NdCl_3 \cdot 4H_2O_{(s)} = NdCl_3 \cdot H_2O_{(s)} + 3H_2O_{(g)}$	7.98141	−9.27	−0.00335	−3507.00	
$NdCl_3 \cdot 3H_2O_{(s)} = NdCl_3 \cdot 2H_2O_{(s)} + H_2O_{(g)}$	7.1613	−9.27		−3346.9	
$NdCl_3 \cdot 2H_2O_{(s)} = NdCl_3 \cdot H_2O_{(s)} + H_2O_{(g)}$	7.97653	−9.27	−0.00503	−3655.41	
$NdCl_3 \cdot H_2O_{(s)} = NdCl_{3(s)} + H_2O_{(g)}$	7.97653	−9.27	−0.00503	−3908.73	
Hydrolysis reaction					
$NdCl_{3(s)} + H_2O_{(g)} = NdOCl_{(s)} + 2HCl_{(g)}$	5.64949	−0.1	−0.69398	−2515.70	−2385.58

vapour pressures for these reactions are shown in Fig. 4. The experimental vapour pressures [14] for the first reaction of Scheme III (reaction 3, Table 1) do not agree with the estimated vapour pressures, nor do they agree with the experimental vapour pressures [15]. Although the experimental vapour pressures [15] do not agree with the estimated vapour pressures for the same reaction, they do agree with the estimated vapour pressure for the first reaction of Scheme I (reaction 1, Table 1).

Equilibrium vapour pressures measured for the first reaction of the dehydration process should be independent of the proposed reaction, assuming that the starting material is pure stoichiometric $NdCl_3 \cdot 6H_2O$. As the measured vapour pressures for the first reaction of Scheme II (reaction 2, Table 1) are in close agreement with those estimated for the first reaction of Scheme I (reaction 1, Table 1), it would appear that the first step in the
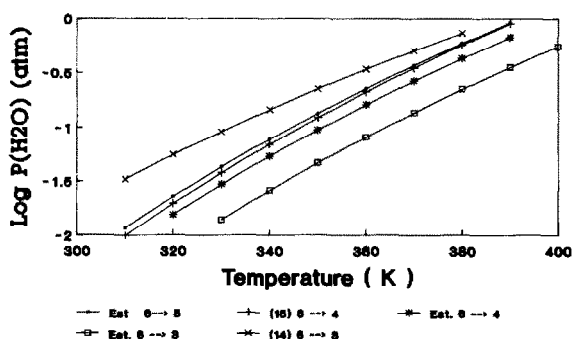

Fig. 4. Equilibrium water vapour pressures for first dehydration step.

dehydration process is as proposed in Scheme I (reaction 1, Table 1), i.e. from the hexahydrate to pentahydrate.

Measured vapour pressures [14] are probably those corresponding to a hydrate other than $NdCl_3 \cdot 6H_2O$, possibly $NdCl_3 \cdot (6.2)H_2O$, as was also the case for other published data [12]. This would account for the difference in experimental vapour pressures measured for the first dehydration step.

Second dehydration step

Three dehydration reactions have been proposed for the second step. These reactions are shown in Table 1 (reactions 4, 5 and 7). Equilibrium vapour pressures from estimated and published [14] data are shown in Fig. 5. The experimental vapour pressures measured for the reaction of Scheme II (reaction 5) do not agree with the estimated values for this reaction, nor do they agree with the estimates for the reaction of Scheme III (reaction 7). Rather, they are in closer agreement with the estimated water vapour pressures for the reaction of Scheme I (reaction 4), i.e. from pentahydrate to tetrahydrate.

The formation of $NdCl_3 \cdot 4H_2O$ during dehydration has been confirmed [9] by DTA. The major phase after the second step of dehydration had an X-ray powder diffraction pattern which matched that for $NdCl_3 \cdot 4H_2O$. This, together with the assumption that the product of the first reaction is $NdCl_3 \cdot 5H_2O$, would seem to indicate that the second dehydration reaction is as proposed in Scheme I (reaction 4, Table 1). Experimental and estimated vapour pressures are in reasonable agreement.

Third dehydration step

Three separate reactions have been proposed for the third dehydration step as shown in Table 1 (reactions 6, 7 and 8). Experimental [15] and
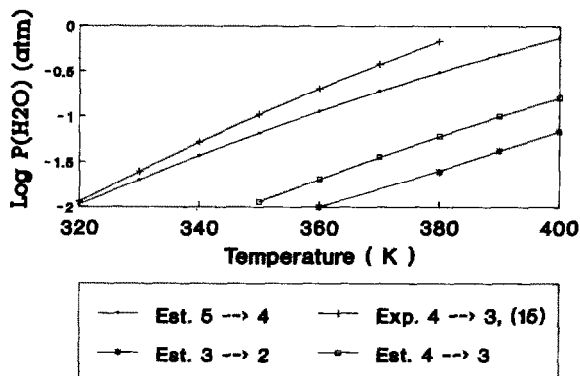

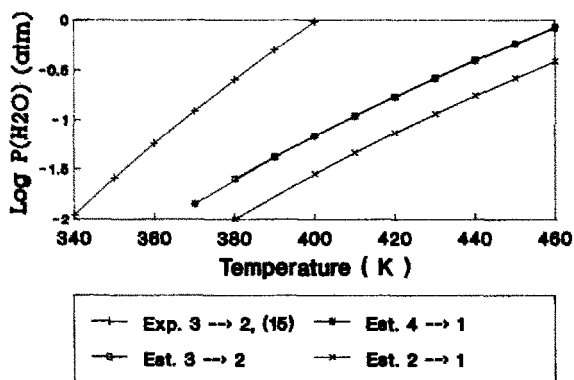Fig. 5. Equilibrium vapour pressures for second dehydration step.

Fig. 6. Equilibrium vapour pressures for third dehydration step.

estimated vapour pressures for these reactions are shown in Fig. 6. There is no agreement between measured and estimated vapour pressures. Estimated vapour pressures for reactions 6 and 7 (Schemes I and II), were calculated independently and are similar by coincidence only.

All three schemes agree that $NdCl_3 \cdot H_2O$ is an intermediate hydrate formed during dehydration. It is not the existence of $NdCl_3 \cdot H_2O$ which is being questioned. Rather, the problem appears to be whether or not an intermediate hydrate is formed between the tetra- and mono-hydrates. As there is no correlation between experimental and estimated vapour pressures, the reaction(s) occurring between the tetra- and mono-hydrates can not be confirmed. It should be noted, however, that the DTA curve from [9] shows no peaks between the tetra- and mono-hydrate peaks.

Fourth and final dehydration steps

Dehydration Schemes I and III consist of four reactions, while five reactions are proposed in Scheme II. Table 1 (reactions 8 and 9) shows the
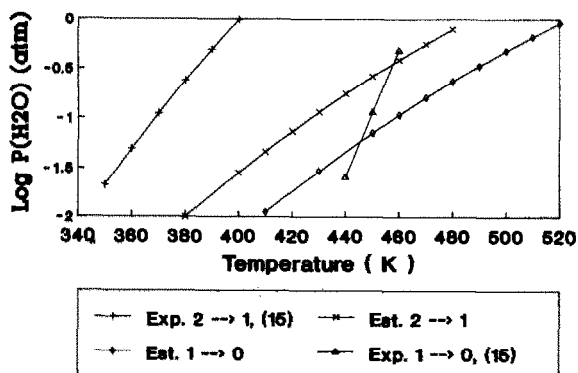

Fig. 7. Equilibrium vapour pressures for fourth and final dehydration step.

fourth and final dehydration reactions for the proposed schemes. As shown in Table 1, all three schemes conclude the dehydration process with the same reaction. Published [15] and estimated equilibrium vapour pressures for these reactions are shown in Fig. 7 where estimated and measured water vapour pressures do not agree for the reactions shown in Table 1. However, hydrolysis reactions [9] occur which involve $NdCl_3$. If hydrolysis was not avoided during the measurements of the water vapour pressures for the final reaction of Scheme II, then the measured vapour pressures would include the contribution from the hydrolysis reactions. This may explain the remarkable deviation of the slope of the experimental vapour pressure curve in comparison to curves for the first three dehydration steps. Although final vapour pressures do not agree, it would appear that the final dehydration reaction is as proposed by all three schemes.

Dehydration reactions with hydrolysis

The equilibrium water vapour pressures published [14,15] for the reactions of Schemes II and III are shown in Fig. 8. Estimated water vapour pressures for Scheme I are shown in Fig. 9. Also included in these figures are the equilibrium vapour pressure ratios of HCl and H_2O for reaction (1), calculated from available data.

In both Figs. 8 and 9, it appears as though simple dehydration of $NdCl_3 \cdot 6H_2O$ will produce pure, anhydrous $NdCl_3$. In both Figs. 8 and 9, the ratio P_{HCl}/P_{H_2O} needed to avoid hydrolysis can be read directly off the scale on the right axis. The hydrolysis reaction (1) is located to the right of
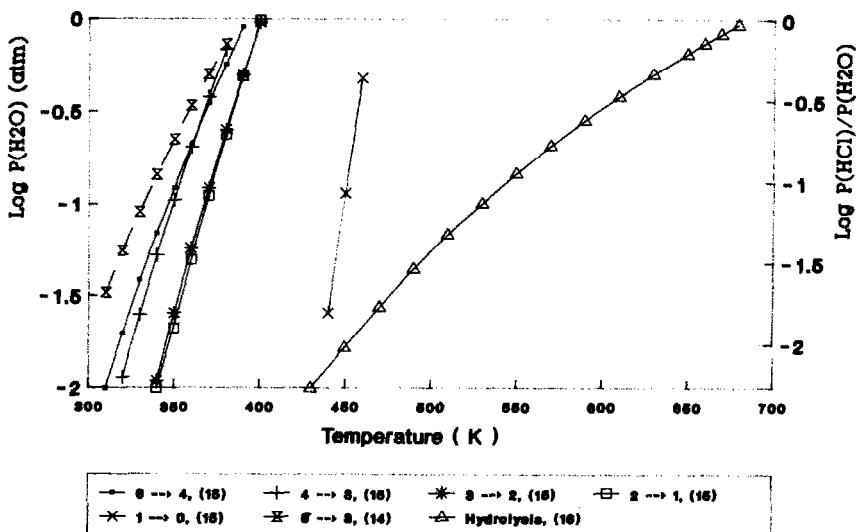

Fig. 8. Equilibrium vapour pressures for dehydration Schemes II and III and hydrolysis.
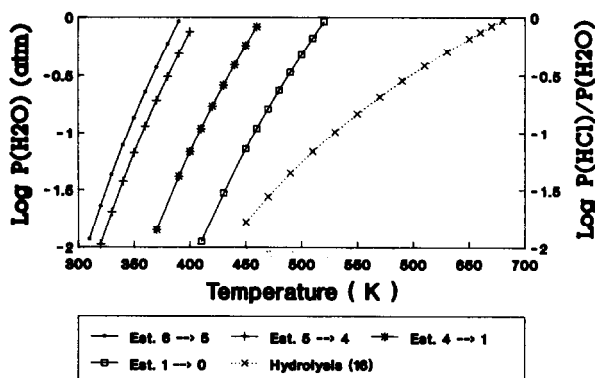
Fig. 9. Equilibrium vapour pressures for dehydration Scheme I and hydrolysis.

the equilibrium vapour pressure curves for the final dehydration reactions in both figures, and this would indicate that hydrolysis by reaction (1) can readily be avoided. Reaction (1) is, however, only one of several possible hydrolysis reactions. As confirmed experimentally [9], hydrolysis may also proceed according to reactions (2) and (3).

The DTA curve generated for the dehydration process [9] contained six peaks, with the fifth peak corresponding to $Nd(OH)_2Cl$. This would indicate that the equilibrium vapour pressure curve for reaction (3) is located between the equilibrium vapour pressure curves for the dehydration reactions that produce the mono-hydrate and the anhydrous salt. In view of this, simple dehydration will not produce anhydrous $NdCl_3$.

The compound $Nd(OH)_2Cl$ decomposes according to reaction (4), and as a result the final product of simple dehydration will always contain some NdOCl. Although this reaction has been identified, the temperature dependence of the heat capacity of $Nd(OH)_2Cl$ is not available, nor is it possible to have it accurately estimated. Thus, equilibrium vapour pressures cannot be calculated.

CONCLUSIONS

Basic thermodynamic data including heat capacities, standard entropies, standard heats of reaction and heats of solution were estimated for all conceivable hydrates of $NdCl_3$. Based on these data, equilibrium water vapour pressures and hydrogen chloride pressures were calculated for all conceivable dehydration reactions.

Comparison of estimated water vapour pressures with published data suggest that dehydration proceeds from hexa- to penta- and then to tetra-hydrate. Dehydration reaction(s) from the tetra- to the mono-hydrate could

not be confirmed. The final dehydration step is probably from the monohydrate to $NdCl_3$ via $Nd(OH)_2Cl$.

Simple dehydration cannot be employed to produce pure, anhydrous $NdCl_3$ and under such conditions, $Nd(OH)_2Cl$ will form, which on decomposition will produce NdOCl.

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