Thermochemistry of **alkalitrichloro-nickelates. Enthalpies of formation by solution calorimetry**

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The enthalpies of solution of a series of alkalitrichloronickelates $ANiCl_3$ (A = Cs, Rb, K, Tl, NH_4) and their constituting chlorides ($NiCl_2$ and ACl) were determined in a medium of 0.1 M HCl at 298 K (for Tl at 323 K) with 1200 H_2O. With these results the enthalpies of formation of the trichloronickelates from the corresponding binary chlorides were calculated.

1. Introduction

The aim of this investigation was to study the relative thermochemical stabilities of trichloronickelates in terms of the enthalpy of formation of the double chloride from the constituting chlorides.

The electrostatic part of the lattice energy can be calculated for the substances under consideration by means of a point-charge model, whereby polarization effects are taken into account. By use of a Born-Haber cycle enthalpies of formation can be estimated. In a subsequent paper the results of these calculations will be given and the trend of the "theoretical" stability obtained by these calculations will be compared with the observed stability sequence Cs > Rb > Tl > K. In practice the enthalpies of solution of the substances can be measured with a calorimeter and from these results the actual enthalpy of formation can readily be deduced. All $ANiCl_3$ compounds have the hexagonal perovskite structure, generally known as the $CsNiCl_3$ structure.

2. Experimental

CALORIMETRIC APPARATUS AND PROCEDURE

For the measurement of the enthalpy of solution a calorimeter of the isoperibol type was used. The calorimeter consists of a silverized glass Dewar vessel. A schematic drawing is given in figure 1. The calorimeter was submerged in a controlled water-bath with temperature fluctuations within ± 0.01 K. For the measurement of the temperature a calibrated resistor with negative temperature coefficient (Philips Type E 205 CE/P) was used, in connection with a Wheatstone bridge circuit. A combined

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stabilized d.c. potential source and unbalance amplifier was used. At the beginning of an experiment the bridge was brought into balance. The change in the resistance of the thermistor during the experiment brought the bridge slightly out of balance. This unbalance, which proved to be directly proportional to the temperature change, was amplified and fed to a recorder. The scale of the recorder was calibrated before every measurement by means of a standard resistor box. The smallest temperature difference observed during the measurements was about 0.05 K. This could easily be measured with a noise level of 1.0 per cent.
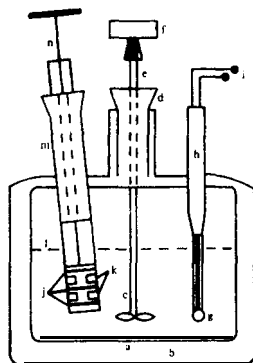

FIGURE 1. Schematic drawing of the calorimeter. a, silverized walls; b, vacuum; c, stirrer; d, bored plug of PTFE; e, flexible shaft; f, synchronous motor; g, thermister in glass tube; h, holder for thermistor; i, connections from thermistor to the bridge; j, "O"-rings; k, sample compartments; l, tube of polythene; m, bored plug of PTFE; n, injector for the piston.

To dissolve the substances into the medium the piston system drawn in figure 1 was used. The piston, made of PTFE, consists of two compartments. This design made it possible to dissolve first the AC1 (in the lower compartment) in 0.1 M HCl solution and after stabilization to dissolve $NiCl_2$ (in the upper compartment) in the AC1 in 0.1 M HCl solution.† This setup corrects for the enthalpy of mixing of the solutions of the binary compounds.

During the measurement a glass stirrer was used, operated by a synchronous motor via a flexible shaft. For the calibration of the calorimeter the enthalpy of solution of KCl in pure water was used: $AH = + 17.217$ kJ mol^{-1} at 298.15 K.[1]

MATERIALS

Anhydrous nickel chloride was obtained by refluxing $NiCl_2 \cdot 6H_2O$ of reagent-grade with thionyl chloride. The anhydrous nickel chloride was filtered from the thionyl chloride solution and dried to remove remnants of thionyl chloride in vacuum at 390 K. The ACl compounds used were of reagent grade and dried in vacuum at 370 K. The double chlorides $ANiCl_3$ were prepared by fusing l-l mixtures of the corresponding reagents in evacuated quartz ampoules. The ammonium compound

† Throughout this paper M = mol dm^{-3}.

however was prepared by evaporation of a solution containing a l-l mixture of $NiCl_2 \cdot 6H_2O + NH_4Cl$. The crystals were then dried in a nitrogen flow in a glass tube at 390 K.

All chemicals used were stored in a dry nitrogen atmosphere in a glove bag, because of the **hygroscopic** nature of most of the compounds. The weighings of the starting materials for the syntheses were performed on a Mettler balance, situated inside the glove bag. The weighings of the samples for the calorimetric measurements and the filling of the compartments of the piston system were also performed inside the glove bag. X-ray powder diffraction patterns showed in all cases the existence of double chlorides, except in the case of $NaCl + NiCl_2$ (which consists of a mixture).

The chloride contents of the compounds were determined by argentometric titration with potentiometric endpoint detection. Nickel was determined by means

TABLE 1. Results for the mass fractions $w(Ni)$ and $w(Cl)$ of Ni and Cl and $10^2 \delta \Delta H_t / \Delta H_t$, the percentage error is ΔH_t generated by titration error

| Compound | $10^2 w(Ni)$ | | $10^2 w(Cl)$ | | $10^2 \delta \Delta H_t / \Delta H_t$ | |
	calc.	found	calc.	found	Ni analysis	Cl analysis
$KNiCl_3$	28.76	28.63	52.09	52.24	6.1	
$RbNiCl_3$	23.43	23.46	42.45	42.30	1.2	2.5
$CsNiCl_3$	19.70	19.75	35.69	35.58	0.9	1.8
NH_4NiCl_3	32.06	31.96	58.08	57.93	6.1	
$TlNiCl_3$	15.89	15.82	28.79	28.68	1.9	4.0

of a complexometric titration with EDTA at $pH = 10$ and murexide as indicator. The analytical results are given in table 1.

To reduce the hydrolysis of the Ni^{2+} ion a medium of 0.1 M HCl was used as solvent in the calorimeter.

3. **Results**

Preliminary experiments were carried out to determine the molar enthalpy of solution of KCl and $NiCl_2$ at various end-concentrations. These experiments showed that $1200H_2O$ yields practically ideal solutions. For the calculation of the molar enthalpy of solution ΔH_{soln} the following expression can be used :

$$\Delta H_{soln} = \varepsilon_c M_s c \Delta R / m_s \Delta_c,$$

where ε_c is the enthalpy equivalent of the calorimeter, M_s the molar mass of solute, c the calibration constant of the recorder output, AR the height of the output signal (so that $c\Delta R$ is the change of resistance of the thermistor), m_s the mass of solute dissolved, and A, the temperature coefficient of the resistance of the thermistor (about 100 Ω K^{-1}). The enthalpy equivalent of the empty calorimeter was determined from the molar enthalpy of solution of KCl in water (its value was about 33.5 J K^{-1}). For the contents, the specific heat capacity of the 0.1 M HCl solution at 298 K we adopted the value 4.155 J $K^{-1} g^{-1}$,[1] and for water at 298 K 4.1798 J $K^{-1} g^{-1}$.[2] During all experiments the same mass of solvent (55 g) was used.

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To obtain from the output of the recorder (resistance against time) the correct "instantaneous" change of resistance of the thermistor, the correction method described by Kubaschewski *et al.*[3] was used. In table 2 the molar enthalpies of solution of the investigated substances and the calculated molar enthalpies of formation are given. The molar enthalpy of solution of $NiCl_2$ in 0.1 M HCl is $-(76.82 \pm 0.42)$ kJ mol^{-1}. From the results in table 2 it follows that the molar enthalpy of mixing of 0.1 M HCl solutions of $NiCl_2$ and AC1 compounds is negligible in comparison with the experimental error.

TABLE 2. Molar enthalpies of solution and of formation at 298 K (for TiCl and TlNiCl$_3$ at 323 K)

AC1	$\dfrac{\Delta H_{soln}(ACl)}{\text{kJ mol}^{-1}}$	$\dfrac{\Delta H_{soln}(NiCl_2)}{\text{kJ mol}^{-1}}$	$\dfrac{\Delta H_{soln}(ANiCl_3)}{\text{kJ mol}^{-1}}$	$\dfrac{-\Delta H_f(ANiCl_3)}{\text{kJ mol}^{-1}}$
NaCl	$+4.44 \pm 0.04$	-76.94 ± 0.42	—	—
KC1	$+17.20 \pm 0.17$	-77.03 ± 0.42	-51.67 ± 0.50	8.16 ± 0.67
RbCl	$+16.40 \pm 0.17$	-77.19 ± 0.42	-33.30 ± 0.38	27.49 ± 0.59
CsCl	$+16.90 \pm 0.17$	-76.94 ± 0.42	-22.30 ± 0.25	37.74 ± 0.54
NH$_4$Cl	115.02 ± 0.17	-77.07 ± 0.42	-52.51 ± 0.50	9.54 ± 0.67
TlCl	141.21 ± 0.38	-77.24 ± 0.42	-17.07 ± 0.17	18.96 ± 0.59

As already mentioned the compound $NaNiCl_3$ does not exist. This was also confirmed with the calorimetric measurement of a fused mixture of $NaCl + NiCl_2$. The curve of temperature against time showed two consecutive temperature effects opposite in sign. The first one was endothermic (dissolution of NaCl) and the second one exothermic (dissolution of $NiCl_2$).

The measurements for $TlCl + NiCl_2$ were performed at 323 K because of the low solubility of TlCl at 298 K.

The molar enthalpies of formation of the double chlorides from the binary chlorides are given by the relation:

$$\Delta H_f = \Delta H_{soln}(ACl) + \Delta H_{soln}(NiCl_2) - \Delta H_{soln}(ANiCl_3).$$

4. Discussion

The observed values for the enthalpies of formation correspond qualitatively with Schmidtz-Demont's rule. This rule states that a binary compound is relatively more stable if the difference between its melting temperature and those of the constituting compounds is smaller. According to the phase diagrams[4, 5] of the investigated systems an increasing stability is expected for the sequence K < Tl < Rb < Cs.

It seems useful to make some comments on the accuracy of the results. Usually much attention is paid to the precision of the calorimetric equipment proper. This can be very high with modern instrumentation and may yield results within a few tenths of a per cent, in terms of purely calorimetric precision. Relatively less attention is given to the purity of the materials under consideration. If chemical analysis of a compound such as ABX_3 yields the theoretical mass percentages of the elements B and X within 0.2 to 0.3 per cent, the material is usually considered to be pure.

It can be shown, however, that errors may arise from this assumption exceeding those of the actual calorimetric measurement. The preparation of $\mathbf{ABX_3}$ from AX and BX, involves as a first step the mixing of equal amounts of substance under a carefully dried nitrogen atmosphere. It turns out however that small amounts of the BX, compound in particular are inevitably lost by electrostatic dispersion so that the ultimate ABX, compound contains a small excess of (heterogeneously mixed) AX. If the formula of the resulting material is assumed to be $x\mathbf{Ax} + (1 - x)\mathbf{ABX_3}$ where $x \ll 1$, then the deviations δw from the theoretical mass fractions w (with respect to x = 0) of the element X and B are given by:

$$\delta w(X) = -x M_X(2M_{AX} - M_{BX_2})S^{-1}, \tag{1}$$

$$\delta w(B) = -x M_B M_{AX} S^{-1}, \tag{2}$$

with $S = M_{ABX_3}^2 \{ 1 - x M(BX_2)/M(ABX_3) \}$, where M denotes molar mass.

Taking $\mathbf{RbNiCl_3}$ (Ni, 23.43 mass per cent; Cl, 42.45 mass per cent) as a typical example the respective deviations $\delta w(Cl)$ and $\delta w(Ni)$ as functions of x are given in the second and third columns of table 3. Based on analytical experience an error of 0.4 per cent in the chemical (titrimetric) analysis of Cl^- and Ni^{2+} was found, so the corresponding errors in $w(Cl)$ and w(Ni) are 0.17 per cent and 0.09 per cent respectively, for pure $\mathbf{RbNiCl_3}$. Comparison with the data in the table shows that it is not possible to make a distinction between $\mathbf{RbNiCl_3}$ and its mixture with 2 moles per cent and 1 mole per cent of RbCl on the basis of Cl- and Ni^{2+} analyses, respectively. Furthermore if $\mathbf{AH_,}$, ΔH_2, and ΔH_3 are the molar enthalpies of solution of pure AX, BX,, and ABX, respectively, the apparent enthalpy of solution of AX containing ABX, is given by

$$AH,, = (1 - \alpha)\Delta H_3, \tag{3}$$

where

$$\alpha = x\{1 - x M(BX_2)/M(ABX_3)\}^{-1}[\{M(AX)/M(ABX_3)\} - (\Delta H_1/\Delta H_3)]. \tag{4}$$

Thus the ratio R of the apparent $\Delta H_{f,a}$ and true $\Delta H_{f,t}$ enthalpy of formation of ABX, from AX and BX, is given by

$$R = \Delta H_{f,a}/\Delta H_{f,t} = 1 + \alpha\Delta H_3/(\Delta H_1 + \Delta H_2 - AH,). \tag{5}$$

Values of R for RbNiCl, are given in the last column of the table 3.

TABLE 3. Deviations δw from the theoretical mass fractions $w(Cl)$ and $w(Ni)$ elements Cl and Ni for $\mathbf{RbNiCl_3}$ as a function of the mole fraction x of excess $\mathbf{RbCl,}$ and corresponding ratios R of the apparent and true enthalpy of formation

x	$10^2 \delta w(Cl)$	$10^2 \delta w(Ni)$	R
0.005	0.032	0.057	1.006
0.01	0.064	0.114	1.012
0.02	0.128	0.229	1.025
0.04	0.259	0.462	1.051
0.06	0.392	0.700	1.081

If, for example, the mean chlorine content of the RbNiCl, is found to be (42.60 ± 0.17) mass per cent, then $\delta w(Cl) = -(0.15 \pm 0.17)$, and the values of R indicate an

uncertainty of about ± 2.5 per cent in the enthalpy of formation, on the basis of the Cl content alone. It is seen that a precise determination of the Ni content is more important than a Cl analysis. Analogous calculations reveal that uncertainties in $\Delta H_{f, t}$ for NH_4^+ and K^+ compounds are larger, and for Cs^+ and Tl^+ compounds are smaller than for Rb^+.

Suppose that the error generated by material impurity must be smaller than 0.5 per cent in the enthalpy of formation (in connection with very accurate calorimetric measurement) then the nickel content must be determined with a standard error of less than 0.15 per cent. This can hardly be achieved with normal standard titration techniques and thus elaborate gravimetric methods must be used.

In table 1 the results of the Cl and Ni analyses of the double chlorides are given and according to the experimental accuracy the materials are pure (within the titration limits). Due to the error in both titration methods, experimentally found to be 0.4 per cent, an uncertainty in *AH,* is generated, given also in table 1. A comparison of table 1 and table 2 reveals that predicted (on analytical data) and observed uncertainty are of the same magnitude.

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