

WHY DO TERNARY COMPOUNDS EXIST? – THERMOANALYTICAL INVESTIGATIONS ON BINARY SYSTEMS OF METAL CHLORIDES

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Ternary chlorides are stable if they can be formed from each pair of the other compounds in a system with a gain in energy. Especially, the energy of formation from the two adjacent compounds, the energy of synproportionation must be negative. At 0 K this condition is fulfilled, if (lattice) enthalpy is won. At higher temperature also the $T \cdot \Delta S$ -term of the Gibbs-Helmholtz-equation can be of significance: a loss in ΔH must be compensated by a gain in $T \cdot \Delta S$, if a (high-temperature) compound shall exist.

This conception was proved experimentally on systems ACl/MCl_2 and $ACl/LnCl_3$ ($Ln =$ Lanthanides). By DTA and X-ray powder patterns the phase diagrams of the pseudobinary systems were elucidated, to yield the stoichiometry and structures of the existing compounds. By solution calorimetry the formation enthalpies at room temperature from the binary parent-compounds were determined. Measurements with a galvanic cell for solid electrolytes at temperatures higher than $\sim 300^\circ\text{C}$ yield the free enthalpies and entropies of synproportionation.

The main result of these measurements is, that compounds with isolated coordination polyhedra ($K_2CoCl_4 =$ tetrahedra; $Rb_3LaCl_6 =$ octahedra) can have a sufficiently high gain in entropy to be stable at temperatures $> 0\text{ K}$.

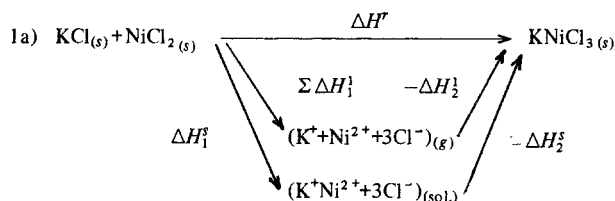
Stability criteria for ternary chlorides

In text-books of solid state chemistry, the treatment of ternary halides is based on the conception of optimal lattice enthalpies: the ions are to be arranged in a way that a maximum of Coulomb-energy is gained. In the hard-spheres approximation, for instance for fluorides, this arrangement depends only on the size and the charge of the ions. Thus, for 1:1-fluorides AMF_3 , which are crystallizing with perovskite-like structures the Goldschmidt's tolerance-factor determines the optimal structural variant. – This conception holds for double chlorides $AMCl_3$ too, but has to be completed by the effect of anion polarization for quantitative purposes [1]. Analogous considerations are applicable for double chlorides of other stoichiometry.

By this treatment a correlation between ionic sizes and structures of existing compounds is obtained, but no answer to the question, why these compounds exist at all; why is the compound $KNiCl_3$, e.g., more stable than a 1:1-mixture of KCl and $NiCl_2$? Remaining in the foregone approximation this will be the case, if the lattice enthalphy of $KNiCl_3$ is more negative,

more exothermic, than the sum of the lattice energies of the binary compounds. As Table 1 demonstrates we can determine these quantities by solution calorimetry [2].

Table 1 Energy values for the formation of KNiCl_3



ΔH^l = lattice enthalpy; ΔH^s = solution enthalpy

1b) *Solution calorimetry*

E.M.F.-measurement

$$\Delta H_1^l(\text{NiCl}_2) = -77.03 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H_1^l(\text{KCl}) = +17.20 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H_2^s(\text{KNiCl}_3) = -51.67 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\text{e.m.f./mV} = 63.8 + 0.1324 \cdot T, \text{K}$$

$$\Delta G^r / \text{kJ} \cdot \text{mol}^{-1} = 6.2 - 0.0128 \cdot T, \text{K}$$

$$\Delta H^r = -6.2 \text{ kJ} \cdot \text{mol}^{-1}; \Delta S^r = 12.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta H^r = -8.2 \pm 0.7 \text{ kJ} \cdot \text{mol}^{-1}$$

If there is existing more than one compound in a system, an additional condition must be fulfilled: Each compound must be stable not only against the decomposition into the binary compounds, but also against the decomposition into any combination of other compounds with the same overall stoichiometry. Especially, the enthalpy for the formation from the two compounds, adjacent in the phase diagram, the enthalpy of synproportionation, must be exothermic, must be negative.

In the late 70's we have measured a lot of such enthalpy differences and have found a surprising feature: They are all very small compared with the absolute values of the lattice enthalpies, in general they are less than one percent. With other words, the ternary compounds exist only by a breath of gained enthalpy!

This feature has two consequences:

- 1) It is nearly impossible to try to calculate such difference in lattice enthalpies with sufficient accuracy.
- 2) The exact criterion for stability are not the enthalpies but the Gibbs-energies or free enthalpies ΔG . Only at T equal 0 K the enthalpies are

the sole factor for stability. — Since the enthalpy differences ΔH° are so small, we can expect additional compounds at more or less higher temperatures — compounds, for which an endothermic ΔH° is compensated by a sufficiently great energy term $T \cdot \Delta S$. These ‘high temperature’ modifications might be stable already at room temperature, which is ‘high’ compared with 0 K. This statement could be proved experimentally, first in the system CsCl/MgCl₂ [3]. Here a compound Cs₂MgCl₄ is formed from Cs₃MgCl₅ and CsMgCl₃ with a loss of 3.0kJ lattice enthalpy.

At this point, the question ‘why do ternary compounds exist?’ gets a new dimension: We now have to investigate the influence of entropy on the stabilities of these compounds or, what is the same, we have to determine free enthalpies in dependence of temperature, in special free enthalpies of synproportionation!

When a reversible galvanic cell can be designed for the process of interest, ΔG can be determined electrochemically by measuring the e.m.f. E of the cell. E is related to ΔG by $\Delta G = -n \cdot F \cdot E$ (n = transported charge: F = Faraday constant). If the dependence of E from T is linear, one can use directly the Gibbs-Helmholtz equation, $\Delta G = H - T \Delta S$, to obtain the enthalpy and entropy too as temperature-independent quantities.

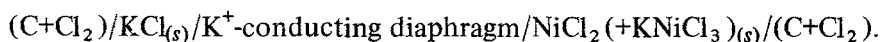
From these reflections a 4-point scheme for investigations can be derived:

1. The phase diagrams of systems ACl/MCl_x must be elucidated by DTA → existence of ternary chlorides and their composition.
2. X-ray-crystallography → structures of the compounds.
3. Solution calorimetry → enthalpies of formation from ACl and MCl_x.
4. E.m.f.-measurements in dependence on T → free enthalpies of reaction ΔG° and reaction entropies ΔS° .

The points 1 to 3 are discussed elsewhere [4]; thus we can concentrate on point 4, the electrochemical measurements.

Free enthalpies of reaction by e.m.f.-measurements

The set-up of the galvanic cell for measuring the e.m.f.’s for the reaction $KCl + NiCl_2 = KNiCl_3$ is:



The electrodes are graphite discs in a chlorine atmosphere. Pressed discs of potassium chloride and nickel(II)-chloride (the latter mixed with some double chloride, to give a reversible cell) are separated by a diaphragm of a potassium-conducting glass.

The cell reaction can be described as follows: At the anode a Cl^- -ion is discharged. For electroneutrality a K^+ -ion passes the separator. Together with a chloride ion formed at the cathode, the compound KNiCl_3 is built up in the nickel chloride disc.

The e.m.f. was measured with a potential follower and recorded with a plotter, either analogue or digital. The temperature dependence of the e.m.f. was measured stepwise in several temperature cycles: the time for each step was between 4 and 10 hours. The collected e.m.f. vs. temperature values were subjected to a linear regression analysis, because in all experiments the temperature dependence of the e.m.f. proved to be linear down to ca. 300° . The upper limit was given by the temperature of the next eutectic. The computer plot gave a line $\text{e.m.f./mV} = a + b T, \text{K}$ with a deflection of ± 0.5 mV. After multiplication with 'minus $n \cdot F$ ', the slope of the line will yield the entropy, the intercept with the ΔG -axis the enthalpy. The result for KNiCl_3 is given in Table 1b. In Table 2 some measured values for 1:1-compounds are compiled. Three features are notable:

- 1) Generally the energy-term, generated by the entropy, is smaller than the enthalpy, but is mostly not negligible.

Table 2 Energy terms ($\text{kJ} \cdot \text{mol}^{-1}$) for reactions $\text{ACl} + \text{MCl}_2 = \text{AMCl}_3$

Compound	Structure	ΔG°	ΔH°	$-(T \cdot \Delta S^\circ)$	ΔH° , calorim.
KCaCl_3	perovsk.	-15.2	-12.2	-3.0	-15.2
KMgCl_3	perovsk.	-14.7	-10.4	-4.3	- 9.9
KMnCl_3	perovsk.	-16.6	-12.0	-4.6	-15.8
KCdCl_3	NH_4CdCl_3	-19.8	(-19.2)	-0.6	-19.2
KCoCl_3	CsNiCl_3	-11.3	- 6.9	-4.5	- 7.0
KNiCl_3	CsNiCl_3	-10.0	- 6.2	-3.8	- 8.16
RbMgCl_3	hex. var.	-28.9	-27.1	-1.8	-23.2
RbCaCl_3	perovsk.	-25.9	-23.1	-2.8	-
RbSrCl_3	perovsk.	- 1.0	+ 5.4	-6.4	+ 3.6
(instable at 298K)		+ 8.1*	+15.5*	-7.4*	-

* values for the synproportionation $0.5 \text{RbCl} + 0.5\text{Rb}_{0.5}\text{SrCl}_{3.5} = \text{RbSrCl}_3$

- 2) The compound RbSrCl_3 has a positive enthalpy of synproportionation. It is stable only at such high temperatures, where $T \cdot \Delta S$ has become greater than $\Delta H'$. This is at 356° .
- 3) The differences between electrochemical enthalpies and those measured by solution calorimetry are sometimes small (KCaCl_3), sometimes greater (KMnCl_3). Such deviations may partially stem from uncertainties of the measurements which do affect ΔH more than the directly measured e.m.f. or ΔG ; but it is more probable that the condition $\Delta C_p = 0$ is not valid down to room temperature. That must be proved by direct C_p -measurements.

In Fig. 1 the results for the system $\text{RbCl}/\text{MgCl}_2$ are given as example for the case that more than one compound is existing.

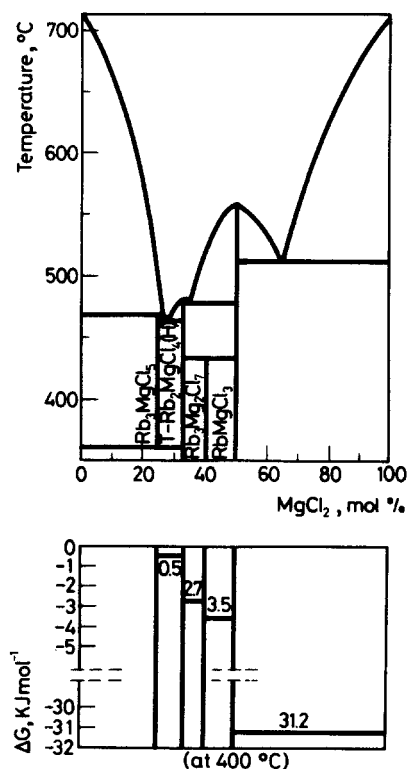


Fig. 1 a) Phase diagram of the system $\text{RbCl}/\text{MgCl}_2$
b) $\Delta G'$ values in the system $\text{RbCl}/\text{MgCl}_2$ at 400°C

The lower diagram shows $\Delta G'$ -values in dependence of composition, measured at 400°: What does this diagram tell us?

- a) If one wants to determine $\Delta G'$ for the formation of RbMgCl_3 from RbCl and MgCl_2 , disks with more than 50 till 100 mol-% MgCl_2 can be used. Going from a composition of 50.1 to 49.9 an abrupt change in e.m.f. is measured.
- b) If a RbCl vs. Rb_3MgCl_5 cell is constructed, the measured e.m.f. must be zero, because the system is empty between 0 and 25 mol-% MgCl_2 . Thus, it can be proved, if in a certain concentration range a compound does exist or not.

Phase diagrams for binary systems at constant pressure are representations of one- and two-phase regions with their phase boundaries, dependent on temperature and concentration. If chemical equilibrium exists the phase regions are zones of minimal Gibbs-energy. With DTA we are measuring enthalpies, which are second-hand quantities, rather than the basic quantities ΔG . The advantage of e.m.f.-measurements can be well demonstrated for the compounds Rb_2MgCl_4 and Rb_3MgCl_5 .

At 421° the former compound reveals a phase transition from the K_2NiF_4 -type with connected octahedra to the K_2SO_4 -type with isolated tetrahedra. The transition temperature is given by the intercept of two e.m.f. vs. T -curves; the one for the formation of Rb_3MgCl_5 from the low-temperature modification of Rb_2MgCl_4 , the other from the high-temperature modification. And this temperature is indeed the equilibrium temperature; for the single values can be measured quasi-isothermally because the time for each temperature step can be prolonged as much as one wants. — By DTA 443° were found from heating curves and 415° from cooling curves, that is a hysteresis of 28°. By general principles of reaction kinetics it is not possible to determine equilibrium temperatures of such reconstructive phase transitions exactly by DTA-measurements!

The compound Rb_3MgCl_5 is stable at temperatures higher than 386°. In a DTA-curve the related effect is found, which indicates that a reaction has occurred. However, it could be a phase transition too. A decision must be found with an additional method, very conveniently by X-ray diffraction. E.m.f.-measurements give both informations directly, for at the decomposition temperature the e.m.f. must be zero.

An analogous behaviour was found for the compound Rb_3LaCl_6 [7]; its decomposition temperature of 444° is used for calibration of our galvanic cells.

Entropy and stability

Good examples for the importance of entropy on the stability of ternary chlorides are the systems ACl/LnCl_3 , ($\text{Ln}=\text{Ln}-\text{Sm}$) we are investigating since 1982. The systems with Cs- and Rb-chloride are very similar, while the K- and Na-systems reveal some specialities, related with the fact that these alkali ions have the same order of size as the lanthanide ions.

For example in the system RbCl/LaCl_3 [6] three compounds exist; two incongruently melting and one, Rb_3LaCl_6 , congruently melting. According to e.m.f.-measurements, this compound with the highest melting point is stable at temperatures above 444° . By DTA temperatures of 450° (heating curve) and 428° resp. (cooling curve) were found. Even when extrapolating the heating rate to zero, an hysteresis of 15° remained.

The compound Rb_2LaCl_5 is formed by a great gain in enthalpy, the entropy-contribution is only small. This compound therefore must be stable at 0 K too. The synproportionation of RbCl and Rb_2LaCl_5 to Rb_3LaCl_6 occurs with a big loss of enthalpy – more than 20 kJ. However, this loss is compensated by a considerable gain in entropy, so that $T \cdot \Delta S$ is equal to ΔH at 444° .

Reaction: $\text{RbCl} + \text{Rb}_2\text{LaCl}_5 = \text{Rb}_3\text{LaCl}_6$;

e.m.f./mV = $537.9 + 0.7502 T, \text{K}$; $\Delta G^r = \Delta G^{\text{syn}} / \text{kJ} \cdot \text{mol}^{-1} = 51.9 - 0.0724 T, \text{K}$;

$\Delta G^{\text{syn}} = 0$ at 717K (444°).

At $T = 298\text{K}$: $\Delta G^r = +30.3 \text{kJ} \cdot \text{mol}^{-1}$, $\Delta H^r = +51.9 \text{kJ} \cdot \text{mol}^{-1}$; $-(T \cdot \Delta S^r) = -21.6 \text{kJ} \cdot \text{mol}^{-1}$.

This entropy gain can be explained in a reasonable kind by the structure of the compound: it has the elpasolit arrangement with isolated octahedra, while RbCl and Rb_2LaCl_5 are consisting of connected octahedra. Thus, the formation of Rb_3LaCl_6 is enlarging the degrees of freedom, the isolated octahedra can oscillate or possibly rotate much easier as if they were connected, the disorder and thus the entropy increases.

The same is true with several compounds of bivalent metals. In Cs_2MgCl_4 we have isolated tetrahedra as in the isotypic K_2CoCl_4 [5]:

For $\text{KCl} + \text{KCoCl}_3 = \text{K}_2\text{CoCl}_4$ $\Delta G^r \text{ kJ} \cdot \text{mol}^{-1} = 2.25 - 0.0245 T, \text{K}$.

Here the change in lattice enthalpy is nearly zero; the compounds exists mainly by the entropy gain.

So we can give an answer to the question in the topic of this article: Ternary chlorides do exist either by a gain in lattice enthalpy and are then stable at 0 K, or they can exist as high-temperature-modifications, if a loss in enthalpy is compensated by a sufficiently great gain in entropy. For a group of compounds the entropy gain can be correlated to structural considerations. These statements could be confirmed by experimental measurements, using a less-common method of thermal analysis.

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Zusammenfassung – Ternäre Chloride sind stabil, wenn sie sich aus allen Paaren der restlichen in einem System existierenden Verbindungen unter Energiegewinn darstellen lassen. Insbesondere muß die Bildungsenergie aus den beiden Nachbarverbindungen, die Synproportionierungsenergie, negativ sein. Bei 0 K ist diese Bedingung erfüllt, wenn dabei (Gitter-) Enthalpie gewonnen wird. Bei höheren Temperaturen kann auch der $T \cdot \Delta S$ -Term der Gibbs-Helmholtz-Gleichung ausschlaggebend werden: ein Verlust an ΔH muß durch einen genügend großen Gewinn an $T \cdot \Delta S$ kompensiert werden, damit eine (Hochtemperatur-) Verbindung existieren kann.

Dieses Konzept wurde experimentell an Systemen ACl/MCl_2 und $ACl/LnCl_3$ ($Ln = \text{Lanthanoid}$) bewiesen. Durch DTA und Röntgenpulveraufnahmen wurden die Phasendiagramme der pseudobinären Systeme erstellt, um Zusammensetzung und Strukturen der existierenden Verbindungen zu ermitteln. Mittels Lösungskalorimetrie wurden die Bildungsenthalpien bei Raumtemperaturen aus den binären Ausgangsverbindungen gemessen. Messungen mit einer galvanischen Zelle für Festelektrolyte bei Temperaturen $>300^\circ\text{C}$ lieferten die freien Enthalpien und Entropien für die Synproportionierungsreaktionen. Als wichtigstes Resultat ergab sich, daß Verbindungen mit isolierten Koordinationspolyedern ($K_2CoCl_4 = \text{Tetraeder}$; $Rb_3LaCl_6 = \text{Oktaeder}$) einen so großen Entropiegewinn aufweisen, daß sie bei hohen Temperaturen stabil sein können.

РЕЗЮМЕ — Третичные хлориды являются стабильными соединениями, если их образование из каждой пары других соединений сопровождается выигрышем энергии. Энергия образования из двух смежных соединений должна быть отрицательной. При 0 К это условие выполняется, если достигнут избыток (решеточной) энтальпии. При более высокой температуре в уравнении Гиббса-Гельмгольца значение приобретает член $T \cdot \Delta S$ таким образом, что потеря в ΔH должна компенсироваться выигрышем в $T \cdot \Delta S$ при наличии высокотемпературного соединения. Эта концепция экспериментально доказана на системах ACl/MCl_2 и $ACl/LnCl_3$, где Ln — лантаноиды. С помощью ДТА и рентгеноструктурного анализа были объяснены фазовые диаграммы псевдобинарных систем с получением при этом стехиометрии и структуры существующих соединений. С помощью калориметрических измерений растворов были определены их энтальпии образования из двойных родственных соединений. Измерения твердых электролитов с гальванической ячейкой при температурах выше 300° дали возможность определить свободные энтальпии и энтропии синпропорционирования. Главным результатом проведенных измерений является тот факт, что соединения с изолированным координационным полиэдром (K_2CoCl_4 — тетраэдр, $RbLaCl_6$ — октаэдр) могут иметь достаточный избыток энтропии, чтобы быть стабильными при температурах выше 0 К.