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THERMAL ANALYSIS BY EMF-MEASUREMENTS ON SOLID ELECTROLYTES

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Galvanic cells of the type $(C+Cl_2)(NaCl_{(s)})(MCl_{2(s)})(C+Cl_2)$ give e. m. f..'s above 280°, which are due to the formation of ternary chlorides Na_nMCl_{n+2}. By the change in slope of continuously measured e.m.f. *vs.* T curves, the temperatures of solid-state reactions in systems $NaCl-MCl_2$ can be found. This method was applied for the systems of NaCl with $NiCl_2$, $CoCl_2$ and $CdCl_2$, and for $KCl-NiCl_2$. With the exception of the system $NaCl-NiCl_2$, all phase diagrams must be corrected.

The formation of ternary chlorides according to the equation

$$n\,ACl + MCl_2 = A_nMCl_{n+2}$$

can have two energetic reasons: 1. a gain in lattice enthalpy; 2. a gain in entropy. However, it is essential that the free (Gibbs) enthalpy of the reaction ΔG_r is negative. ΔG_r can be determined by measuring the e.m.f. of the galvanic cell $(Cl_2 + C)(ACl_{(s)})A^+$ –conducting diaphragm$(MCl_{2(s)})(C + Cl_2)$, making use of the relation $\Delta G_r = -n \cdot F \cdot$ e.m.f. In a previous paper we reported the thermodynamic state functions of the compounds in the system $NaCl-CdCl_2$ [1] as determined by measuring the temperature-dependence of the e.m.f. (For a description of the cell used see [2].)

We found that the time needed to reach the equilibrium potentials at the electrodes can be 2—20 hours, and 0.5—2.0 hours when the temperature is changed. Therefore, the change in e.m.f. as a function of T should be measured stepwise; continuously measured e.m.f. *vs.* T curves show a delay. In general, the e.m.f. is a linear function of the temperature. This was also confirmed by c_p measurements [1]. However, below a certain temperature limit there is a deviation from linearity. This limit depends on the conductivity of the electrolytes, mainly of the alkali metal chlorides. It was found to be ~280° for NaCl and ~350° for KCl. The upper temperature limit is given by the onset of melting, i.e. the temperature of the next eutectic in the system.

In spite of the above mentioned thermal lag of e.m.f. *vs.* T curves, it should be possible to utilize continuous measurements as a method for thermal analysis (TA), for solid-state reactions will cause a change in the slope of such curves at the reaction temperature, and at the eutectic temperature the potential difference should disappear.

In this work the usefulness of the continuous measurement method was checked by applying it to reinvestigate the phase diagrams of $NaCl-NiCl_2$, $KCl-NiCl_2$, $NaCl-CoCl_2$, and $NaCl-CdCl_2$.

Experimental

The apparatus for the TA measurements (Fig. 1) was the same as the one used for the determination of the thermodynamic state functions [1].

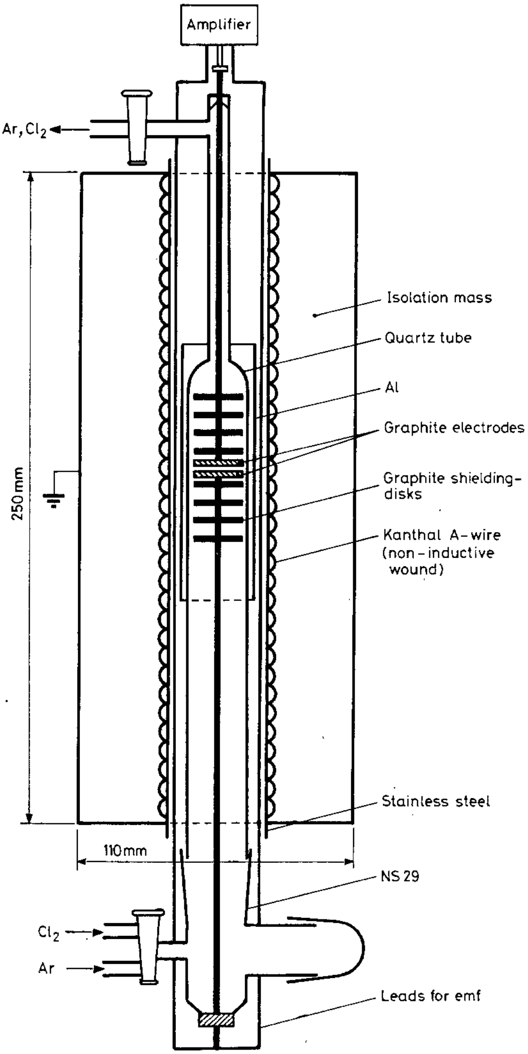


Fig. 1. Apparatus for e.m.f. measurements on solid electrolytes

The anode and cathode are graphite disks (20 mm ϕ) in Cl_2 atmospheres. For a reaction $ACl + MCl_2 = AMCl_3$, the electrode processes are:

$$\text{Anode:} \quad ACl \xrightarrow{-e^-} A^+ + 1/2\, Cl_2 .$$

$$\text{Cathode:} \quad A^+ + MCl_2 + 1/2\, Cl_2 \xrightarrow{+e^-} AMCl_3$$

The sample disks – the electrolytes – were prepared by compressing ACl and MCl_2 (together with some $AMCl_3$ for reversibility), moisture being excluded, similarly to the procedure used in IR spectroscopy. In general, it was not necessary to use any separator; the interface between the two disks behaved like an A^+-conducting diaphragm.

The rate of heating was generally $15° \cdot h^{-1}$. The temperature was measured with a shielded Ni/CrNi thermocouple placed between the quartz and Al tubes. The e.m.f. *vs.* T curves were registered on a strip-chart recorder.

The apparatus for DTA measurements was described previously [3].

Results

The system NaCl–NiCl$_2$

It has been found by DTA [4] that there is no compound at all in this system, the eutectic is at 563°. Accordingly, all $NaCl/(NiCl_2 + NaCl)$ samples of various compositions yielded e.m.f.'s equal to zero at temperatures >280°.

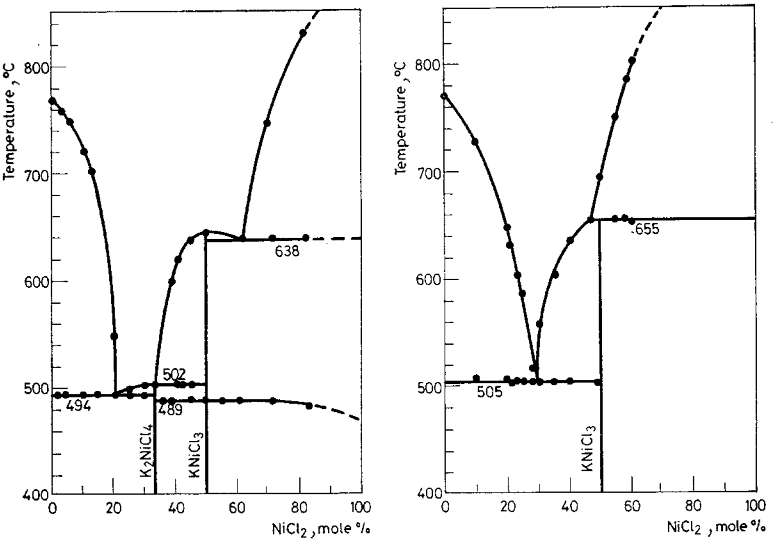


Fig. 2. The system KCl–$NiCl_2$

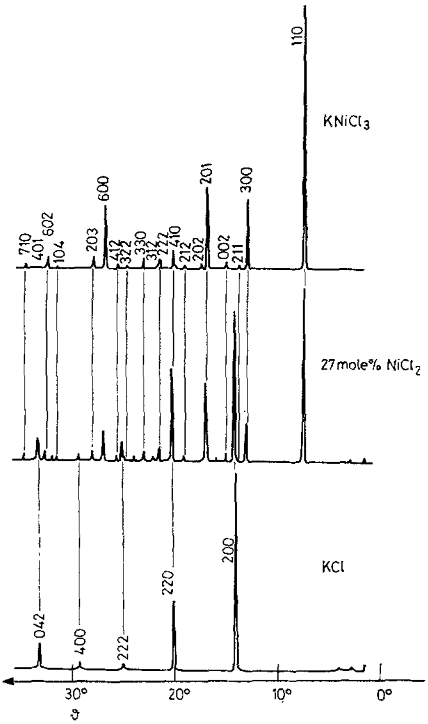


Fig. 3. X-ray goniometer patterns for crystal powders of the system KCl—$NiCl_2$

The system KCl–NiCl₂

By DTA (Fig. 2) Bolshakov [5] found two compounds: K_2NiCl_4 and $KNiCl_3$, the latter with a phase transition at 489°.

In contrast to the reported existence of K_2NiCl_4, cells of the type KCl/($KNiCl_3$ + + K_2NiCl_4) gave e.m.f.'s of zero at each temperature, whereas cells with more than 50 mole % $NiCl_2$ as catholyte gave e.m.f.'s of about 120 mV (above a temperature limit of 390°). No break in the e.m.f. *vs.* *T* curve was observed at 489°.

A reinvestigation of the system yielded the phase diagram shown on the right side of Fig. 2. In agreement with the e.m.f. measurements and also with X-ray patterns, only the compound $KNiCl_3$ exists, with an incongruent melting point of 655°.

By dynamic high-temperature X-ray techniques Dutch scientists [6] found a structural transformation at 290°. They also determined the crystal structures of both modifications.

The system NaCl–CoCl₂

Bolshakov [5] reported that the system contains only one compound, Na_2CoCl_4, which is stable up to 350°. Therefore, e.m.f. measurements should give values different from zero in the temperature range between 280 and 350°.

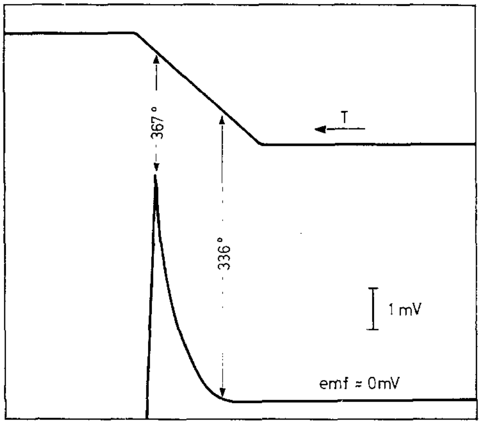


Fig. 4. E.m.f. *vs.* *T* curve of NaCl/(50 mole% $CoCl_2$ and NaCl)

The measured curve was different (Fig. 4): e.m.f. = 0 up to 338°; e.m.f. >0 from 338 to 366°; breakdown of the potential difference at 366°. Consequently, Na_2CoCl_4 is stable only in the temperature range between 338 and 366°. This could be confirmed by a reinvestigation of the phase diagram by means of DTA (Fig. 5).

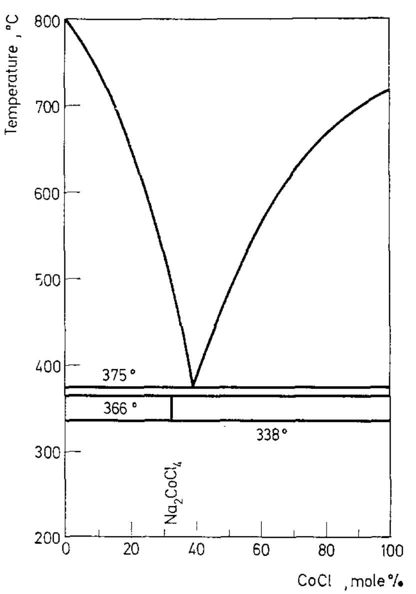


Fig. 5. The system NaCl—$CoCl_2$

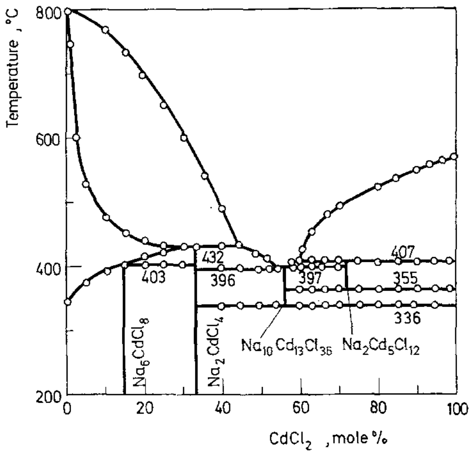
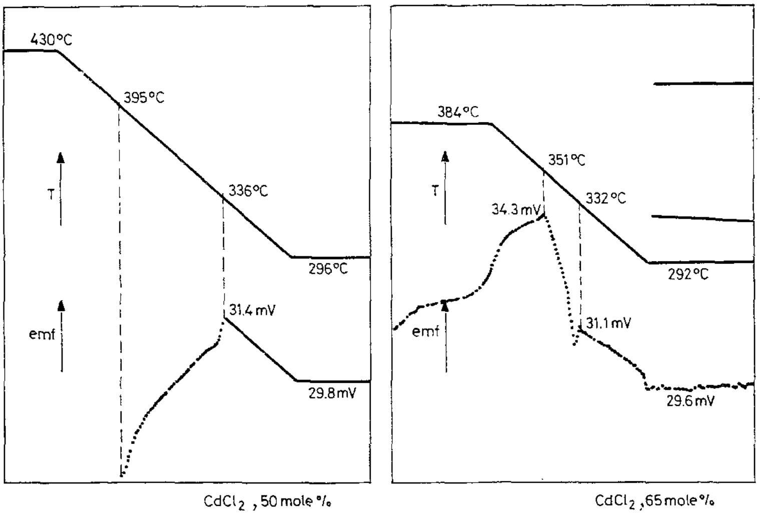


Fig. 6. The system NaCl– $CdCl_2$

Metastable Na_2CoCl_4 can be obtained by quenching. Heating such a sample gives a strong exothermic peak at ~200°.

The system NaCl – $CdCl_2$

The corrected phase diagram (Fig. 6) was described previously [2]. There had been considerable difficulty in determining the compositions of the two $CdCl_2$-rich



$CdCl_2$, 50 mole % $CdCl_2$, 65 mole %

Fig. 7. E.m.f. *vs.* *T* curves in the system NaCl– $CdCl_2$

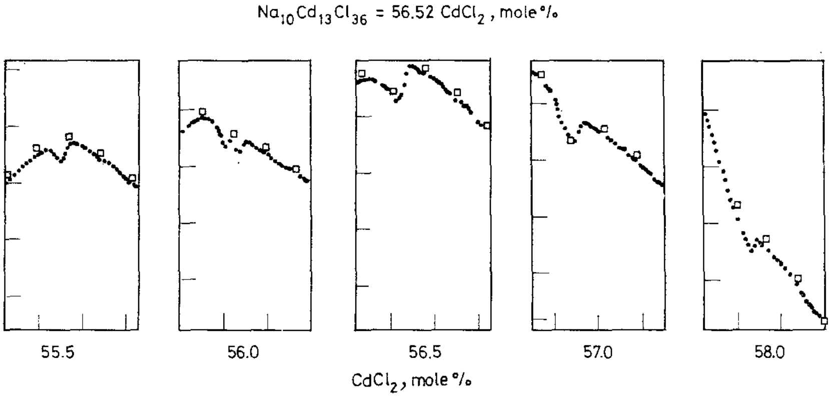


Fig. 8. E.m.f. *vs.* *T* curves near $Na_{10}Cd_{13}Cl_{36}$ in the region of 336°

compounds, because they are formed in a peritectic reaction from the melt and are stable only at higher temperatures.

The application of e.m.f. measurements for solving this problem will be described for $Na_{10}Cd_{13}Cl_{36}$ (56.2 mole% $CdCl_2$).

Figure 7 shows two e.m.f. *vs.* *T* curves, the left one characteristic for the combination of NaCl disks with disks of a composition between 33.33 and 56.52 mole% $CdCl_2$, the right one for >56.52%. The most obvious difference is the change in slope at 332°/336°. Several measurements on samples with an increasing content of $CdCl_2$ gave curves of the type shown in Fig. 8. The characteristic change in slope occurs between 56.5 and 57.0 mole% $CdCl_2$. The formula $Na_{10}Cd_{13}Cl_{36}$ was derived from e.m.f. *vs.* *T* measurements and from preliminary X-ray structure investigations. The structure investigations revealed a relationship between $Na_{10}Cd_{13}Cl_{36}$ and the ilmenite structure of a hypothetical $NaCdCl_3$. In the twofold ilmenite cell with $Na_{12}Cd_{12}Cl_{36}$, two Na^+ are substituted by one Cd^{2+} and a vacancy, resulting in $Na_{10}Cd_{13}\square Cl_{36}$. In a similar way, the composition of the second compound was found to be $Na_2Cd_5Cl_{12}$ or $Na_6Cd_{15}\square_3Cl_{36}$. Within the range of existence of $Na_2Cd_5Cl_{12}$, i.e. >355° and >56.52 mole% $CdCl_2$, it was impossible to make e.m.f. measurements without using an A^+-conducting separator. Without a diaphragm, the e.m.f. dropped slowly to zero, whereas the conductivity increased to 15 times of its normal value. After the measurement, the disks were found to be sintered together. These effects are assumed to be due to a highly increased diffusion of cations caused by the lattice vacancies.

There is evidence that the compound $Na_2Cd_5Cl_{12}$ is only metastable. Working with a separator – we used β-alumina disks – the initially measured e.m.f., fo rinstance at 384°, decreases during ~2 days to a lower value, which depended on the composition. This might be due to an existing mixed-crystal region as equilibrium state.

Discussion

The main advantage of this new TA method is that the e.m.f. is an *intensive* quantity and not an extensive one as ΔH, measured in normal TA. Thus, there is no need to integrate peak areas to obtain the desired thermodynamic functions. The reaction temperature does not have to be constructed from the peak shape, but is given by a kink break in an otherwise linear curve. The heating rate can be as low as wanted, and overheating can easily be avoided.

The main disadvantage is the limitation in temperature and the fact that the measurements are limited to solid-state reactions.

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Zusammenfassung — Mit galvanischen Zellen des Typs $(C + Cl_2)/NaCl_{(s)}/MCl_{2(s)}/(C + Cl_2)$ lassen sich oberhalb 280° EMK's messen, die auf der Bildung ternärer Chloride Na_nMCl_{n+2} beruhen. Durch die Änderung der Steigung kontinuierlich gemessener EMK- gegen T-Kurven lassen sich in Systemen $NaCl/MCl_2$ die Temperaturen von Festkörperreaktionen nachweisen. Diese Methode wurde auf die Systeme des NaCl mit $NiCl_2$, $CoCl_2$ und $CdCl_2$ sowie auf das System KCl—$NiCl_2$ angewendet. Alle Phasendiagramme, mit Ausnahme des Systems NaCl—$NiCl_2$, mußten auf Grund dieser Messungen revidiert werden.

Резюме — Гальванические ячейки типа $(C + Cl_2)/NaCl_{тв.}/MCl_{2тв.}/(C + Cl_2)$ выше 280 °C показали э. д. с, которая возникает в результате образования тройных хлоридов Na_nMCl_{n+2}. На основе изменения наклона кривой на графике э. д. с — температура, были определены температуры твердотельных реакций в системах NaCl—MCl_2. Метод был применен для систем NaCl с $NiCl_2$, $CoCl_2$, $CdCl_2$ и для системы KCl—$NiCl_2$. За исключением системы NaCl—$NiCl_2$, все другие фазовые диаграммы должны быть исправлены.