

## E.M.F. MEASUREMENTS ON SOLID ELECTROLYTES— A TOOL FOR INVESTIGATING SYSTEMS WITH ALKALI METAL CHLORIDES

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### ABSTRACT

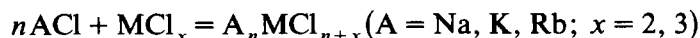
By means of a galvanic cell, e.m.f. values can be measured as a function of temperature for solid reactions of the type  $n\text{ACl} + \text{MCl}_x = \text{A}_n\text{MCl}_{n+x}$  ( $\text{A} = \text{Na, K, Rb}$ ;  $x = 2, 3$ ) and all thermodynamic functions for the reaction can be obtained. Further, this method is a good means of proving the existence or the metastability of compounds and for the determination of exact reaction temperatures.

### INTRODUCTION

The most common way of detecting solid-state reactions is to measure the enthalpy of reaction by DTA. However, whether a reaction occurs is not directed by the enthalpy but by the Gibb's free enthalpy,  $\Delta G^r$ . When a reversible galvanic cell can be designed for the process of interest,  $\Delta G^r$  can be measured directly electrochemically [1]. The equation to be used is

$$\Delta G^r = -nFE$$

where  $n$  = transported charge,  $F$  = Faraday constant and  $E$  = e.m.f. This equation relates the e.m.f. with the Gibb's free enthalpy of reaction, in our investigations with solid-state reactions of the type



The chemical work released by the formation of ternary chlorides is converted into electric energy measured in a galvanic cell or battery.

### PRINCIPLE OF THE METHOD

Figure 1 shows the galvanic cell that was used for studying the formation of  $\text{KMnCl}_3$  from potassium chloride and manganese(II) chloride. The anode

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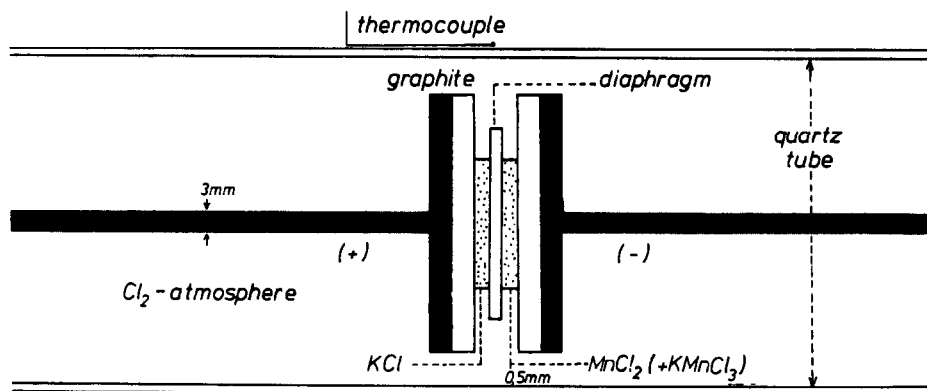
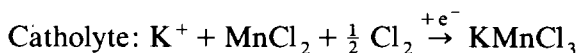
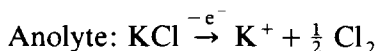


Fig. 1. Galvanic cell for the reaction  $\text{KCl}_{(s)} + \text{MnCl}_{2(s)} = \text{KMnCl}_{3(s)}$ .

and cathode are graphite discs in a chlorine atmosphere. Pressed discs of potassium chloride and manganese(II) chloride (the latter mixed with some  $\text{KMnCl}_3$  to give a reversible cell) are separated by a diaphragm of a potassium ion-conducting glass.

The cell reaction can be described as follows:



At the anode one  $\text{Cl}^-$  ion is discharged. For electroneutrality one  $\text{K}^+$  ion passes the separator. Together with one chloride ion formed at the cathode, the compound  $\text{KMnCl}_3$  is built up in the manganese(II) chloride disc.

The e.m.f. was measured with a potential follower and recorded with a plotter, either analogue or digital. A cross-section of the apparatus is shown in Fig. 2. The temperature dependence of the e.m.f. was measured either stepwise in several temperature cycles or continuously, accepting a certain thermal lag in the e.m.f. vs. temperature curve. The collected e.m.f. 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.  $300^\circ\text{C}$ . The upper limit was given by the temperature of the lowest adjacent eutectic.

## APPLICATIONS

One can detect if in a certain range of concentrations in a two-component system a compound exists or not [2]. In the system  $\text{KCl}/\text{NiCl}_2$  Bolshakov et al. [3] found two compounds,  $\text{K}_2\text{NiCl}_4$  and  $\text{KNiCl}_3$ , the latter with a phase

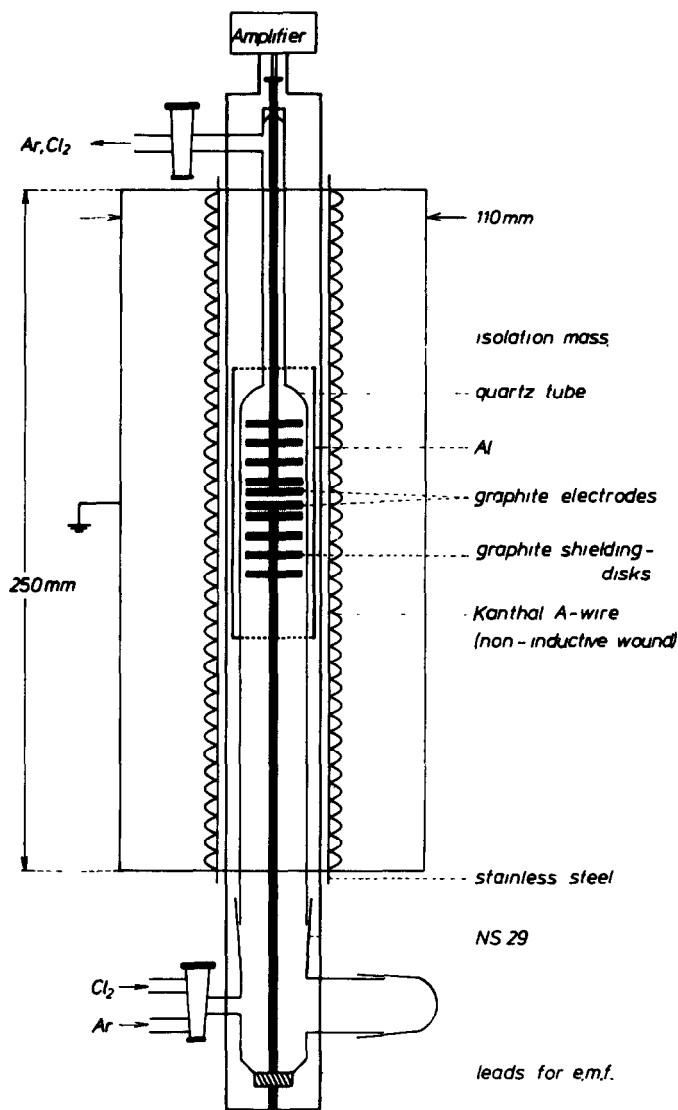


Fig. 2. Cross-section of the apparatus.

transition at  $489^{\circ}\text{C}$ . In contrast, cells of the type  $\text{KCl}/(\text{KNiCl}_3 + \text{K}_2\text{NiCl}_4)$  gave e.m.f.s of zero at each temperature, whereas cells containing more than 50 mole-% of  $\text{NiCl}_2$  as catholyte gave e.m.f.s of about 120 mV (above a temperature limit of  $390^{\circ}\text{C}$ ). No break in the e.m.f. vs. temperature curve was observed at  $489^{\circ}\text{C}$ . A reinvestigation of the system by DTA and high-temperature X-ray techniques and a recent DTA investigation by Bazhenov et al. [4] confirmed these e.m.f. results.

Measurement of the e.m.f. as a function of  $T$  yields all three basic thermodynamic functions with good values for  $\Delta G$ . This is demonstrated in

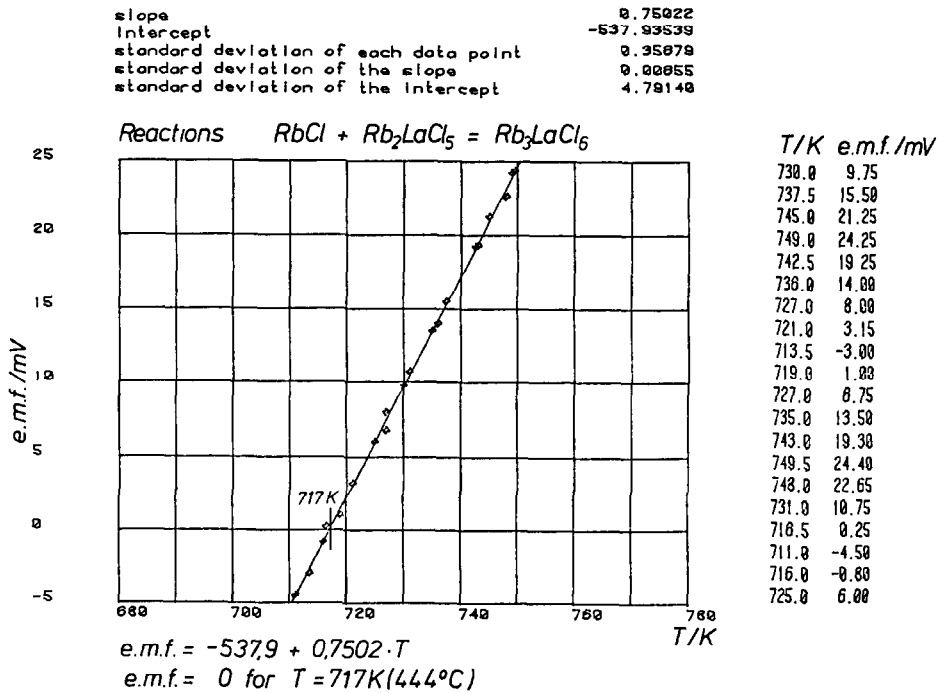


Fig. 3. Computer plot of e.m.f. vs. temperature for  $Rb_3LaCl_6$ .

Fig. 3 for  $Rb_3LaCl_6$  in the system  $RbCl/LaCl_3$  [5]. From  $\Delta G = -nFE$  and  $(\partial\Delta G/\partial T)_p = -\Delta S$  the entropy is obtained, and from the Gibbs-Helmholtz relationship ( $\Delta G = \Delta H - T\Delta S$ ) the enthalpy is obtained as a less accurate function. Because of the linear dependence of  $\Delta G$  on temperature,  $\Delta S$  is obtained as the slope of the regression line and  $\Delta H$  as the intercept with the  $\Delta G$  axis.

### Evaluation



Samples: two with 30 mol-%  $LaCl_3$ ;  $T = 710-750$  K

$$e.m.f./mV = -537.9 + 0.7502T/K$$

$$\Delta G^r/kJ\ mol^{-1} = 51.9 - 0.0724T/K (\pm 0.1\ kJ\ mol^{-1})$$

$$\Delta H^r = +51.9 \pm 0.5\ kJ\ mol^{-1} \quad \Delta S^r = 72.4 \pm 0.6\ J\ K^{-1}\ mol^{-1}$$

$$\Delta G^r = 0\ \text{at}\ 717\ K\ (444^\circ C).$$

Utilizing the  $\Delta G^r$  values of the other compounds in the system,  $Rb_2LaCl_5$  and  $RbLa_2Cl_7$ , the functions for the formation from  $RbCl$  and  $LaCl_3$  also can be calculated.

One can find out if a compound is stable or metastable. With  $Rb_3LaCl_6$   $\Delta G^r$  becomes 0 at 717 K and positive at lower temperatures; now the

“chemical energy” of the decomposition to  $\text{RbCl}$  and  $\text{Rb}_2\text{LaCl}_5$  is generating the e.m.f., which with a negative sign is an indicator of the metastable state (note: a negative e.m.f. gives a positive  $\Delta G^\ddagger$ ). Other examples of such behaviour, recently investigated, are the compounds  $\text{K}_3\text{CeCl}_6$  [6],  $\text{Rb}_3\text{MgCl}_5$  and  $\text{RbSrCl}_3$  [7] and  $\text{K}_{2.08}\text{Ba}_{0.96}\text{Cl}_4$  [8]. In the system  $\text{NaCl}/\text{CdCl}_2$  [1] the situation is more complicated; here  $\text{Na}_{0.77}\text{CdCl}_{2.77}$  decomposes to a mixture of  $\text{CdCl}_2 + \text{Na}_2\text{CdCl}_4$ , which in a cell together with  $\text{NaCl}$  does not yield a  $\Delta G^\ddagger = 0$  but the  $\Delta G^\ddagger$  for the formation of  $\text{Na}_2\text{CdCl}_4$  from  $\text{NaCl}$  and  $\text{CdCl}_2$ .

Exact thermodynamic temperatures of reaction can be determined. As an example we can again take the decomposition reaction of  $\text{Rb}_3\text{LaCl}_6$  at  $444^\circ\text{C}$  (717 K). We found a temperature of  $452^\circ\text{C}$  by DTA and  $437^\circ\text{C}$  from cooling curves. These differences are due to the retarded rearrangement of ions in such “reconstructive phase transitions”. With  $\text{K}_{2.08}\text{Ba}_{0.96}\text{Cl}_4$  no DTA effect was found in cooling experiments.

## DISCUSSION

The main advantage of this new thermal analysis method is that the e.m.f. is an intensive quantity and not an extensive one as is  $\Delta H$  measured in normal thermal analysis. Hence 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 in an otherwise linear curve. The heating rate can be as low as desired, and overheating can easily be avoided. The main disadvantage is the limitation on temperature and the fact that the measurements are limited to solid-state reactions.

In 1980, Wendlandt described a “thermovoltaic detector” (TVD) for the thermal analysis of decomposition reactions [9]. Substances such as  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , when sandwiched between two dissimilar metal electrodes, generate spontaneously an e.m.f. during the thermal decomposition, similarly to Volta’s frog’s leg experiment. However, because the source of this e.m.f. cannot be described quantitatively, one is acquiring only sporadic information; the determination of physical quantities is not yet possible.

## ACKNOWLEDGEMENTS

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