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PHASE DIAGRAM STUDIES OF CHLORIDE SYSTEMS - COMMON AND NOT-SO-COMMON METHODS

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SUMMARY

Phase diagrams are generally generated by DTA-measurements. To obtain equilibrium the samples must often be pre-treated by annealing. If the thermal effects are too weak in the case of displacive solid state reactions, more sensitive methods must be applied additionally. It is demonstrated how EMF-measurements with galvanic cells for solid electrolytes can be used for systems ACl/MCl_x to detect slow reactions of the reconstructive type.

INTRODUCTION

Phase diagrams for binary systems at constant pressure are representations of one- und 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 ΔG. To generate a phase diagram means to detect all phase boundaries. In general, this is done by measuring heating and cooling curves by means of DTA. Thus, the enthalpy of phase reactions is utilized, which is related to the free enthalpy, ΔG, by the heat capacity.

Unfortunately, the enthalpy change tells us nothing about the kind of reaction by which it is generated. Therefore, today it is usual to support the results of DTA by additional methods. In the 100th-anniversary edition of this journal (ref. 1) we have reported own results concerning these objects taken from investigations of systems ACl/MCl_x (A= Na-Cs). Examples, also considered in this paper, are cited together with the page in [1].

SOLID-LIQUID TRANSITIONS

In fig. 1 all solid-liquid transitions, exept those of mixed crystals formation, are displayed together with the correlated ΔT-traces.

To avoid undercooling the values for the liquidus curves are generally taken from heating experiments: Thus, T_1 is the 'peak

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temperature' of the melting process. However, the correct melting temperature for the compound, T_y, is taken from the 'extrapolated onset'. Thus, one is abruptely changing the kind of evaluation, the result is a sinusodial curve (see [1], p. 94). With other words: the liquid temperatures near a congruently-melting compound are to high! One can avoid this error by taking the onset-temperatures from cooling curves, using a sufficently large sample to prevent errors by undercooling.

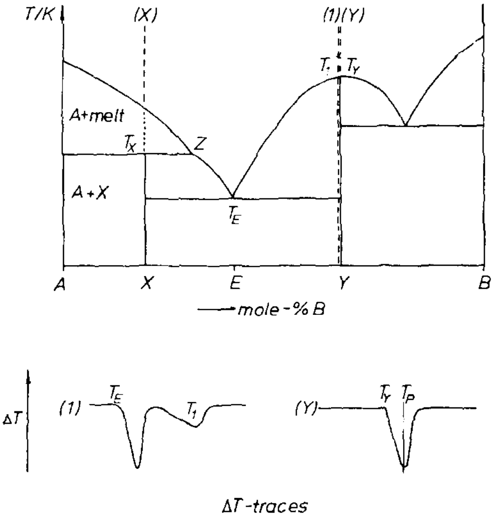

Fig. 1. Hypothetical binary system.

Another source of errors arises in the case of incongruently-melting compounds: during the freezing of the melt X sedimentation of the formed solid can occur. Thus, the rest-melt becomes richer in B and one will find the 'wrong' eutectic at T_X additionally. - One can avoid this mistake which leads to a wrong composition of the compound, by quenching the melt with subsequent annealing short below T_X.

SOLID-SOLID TRANSITIONS

From a structural point of view we have to distinguish reconstructive and displacive phase transitions.

Reconstructive means that the topology of the arrangement of ions is drastically changed. Thus the activation energy is anticipated to be high, the differences between DTA- and equilibrium temperature should be large. Solid state reactions - the formation or decompositions of compounds in the solid state - can be considered as a special kind of reconstructive transitions. In displacive transitions the ions are only a little shifted, avtivation energy and temperature difference are expected to be rather small.

There exist two significant sources of errors:

1. In displacive transitions the heat of transition can be so small that only a very small thermal effect results.

2. For a reconstructive phase transition the activation energy can be so high that one will find considerable amounts of overheating and undercooling; the result is a big hysteresis between heating and cooling curves in DTA.

Displacive phase transitions

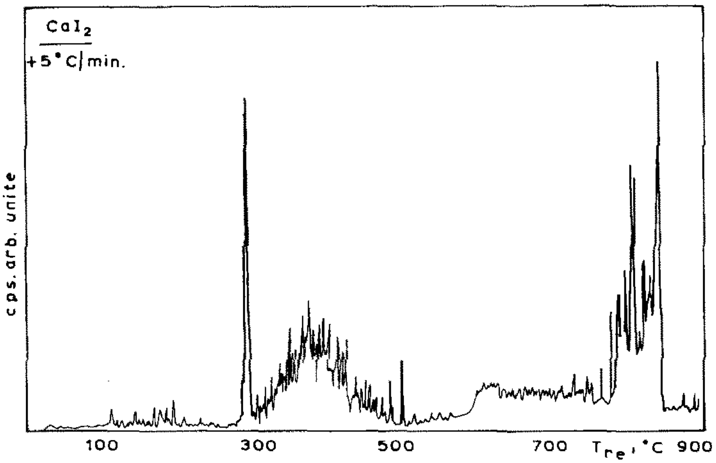

Fig. 2. Thermosonigram for CaI_2

If a thermal effect in DTA is to small, one will try to find more sensitive methods.
One of those methods, very well known among thermal analysists, is the thermosonimetry (ref.2): the 'noise' of a solid state reaction is measured with a stethoscope. In fig. 2 a thermosonigram (Dr. Lønvik, Trondheim) is shown for a phase transition, we had found for CaI_2 at 280°C (ref.3). It is indicated by a sharp peak; the sluggish effects ~360°C might be related to the curing of lattice defects. This method is very sensible, but tells us nothing about the kind of reaction.
The most powerful tool not only for detecting phase transitions but also for recognizing the structural change is the X-ray crystallography! Generally, one compares powder patterns of quenched or normally cooled samples with those of the starting compounds. New, additional reflections indicate new compounds. To ensure the stoichiometry one can try to solve the structure of the new compound by indexing each single reflection.
For detecting phase transition it is favourable to use the dynamic high-temperature Guinier-technique. Here a film is moved related to the temperature change. An example is given in [1], p. 90.
If the difference of the X-ray patterns is becoming too small - transition

from monoclinic to orthorhombic $RbCdCl_3$, e.g. (ref.4) - one can try to use methods which are more sensitive for changes in symmetry. Some of them are:

1) to measure the dependence of birefringence from temperature. By this method Arend et al. (ref.5) detected three transitions for Rb_2ZnCl_4 between 5 and 350K. The two lower one were also established by

2) measurement of the dielectric constants.

3) ^{81}Bromium nuclear quadupole resonance was applied for finding the low temperature transitions of Cs_2HgBr_4 (ref.6).

4) Two of the transitions at 170K and 230K were also detected by measuring the temperature dependence of elastic constants.

5) Kobayashi et al. (ref.7) have investigated $[N(CH_3)_4]_2ZnCl_4$, doped with Mn^{2+}-ions, by means of electron spin resonce. The hyperfine-structure revealed five transitions in the range -117 to 23°C.

Better known methods are:

6) c_p-measurements. (Rb_2ZnCl_4; Chihara et al. (ref.8)).

7) electric conductivity measurements (Li_2MnCl_4; Lutz et al. (ref.9)).

Reconstructive phase transitions

In the system $RbCl/LaCl_3$ (ref.10) a compound Rb_3LaCl_6 is existing which is stable at temperatures higher than 444°C. As fig. 3 indicates the reaction temperature taken from heating curves is too high and too low from cooling curves. A hysteresis is still existing when extrapolating to the heating rate zero.

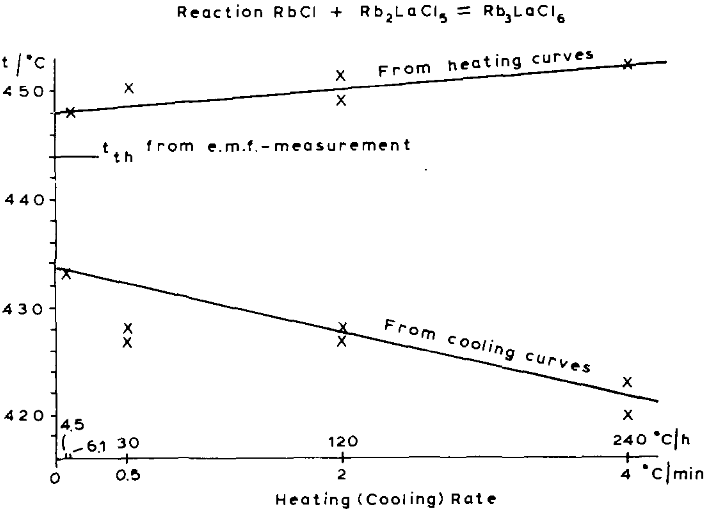

Fig. 3. Reaction temperature for Rb_3LaCl_6

The thermodynamic (equilibrium) temperature was determined with a self-developed galvanic cell for solid electrolytes. A detailed description is given elsewhere (ref.11). For a reaction $ACl+MCl_x=AMCl_{x+1}$ the set-up of the cell is:

$(C+Cl_2)/ACl/A^+$-conducting glass/$MCl_x(+AMCl_{x+1})/(C+Cl_2)$

Anode and cathode are graphite disks in a Cl_2-atmosphere. Pressed disks of ACl- and $MCl_x(+AMCl_{x+1})$-powder are separated by an A^+-conducting diaphragm. The cell reactions is: At the anode one Cl^- is discharged. For electroneutrality one A^+ passes the diaphragm. Together with one chloride-ion, formed at the cathode, the compound $AMCl_{x+1}$ is built up in the MCl_x-disk. The E.M.F. of the cell, measured with a potential follower, is related to the Gibbs enthalpy ΔG^r for the solid state reaction by $\Delta G^r=-n\cdot F\cdot EMF$. The temperature dependence of the EMF was measured stepwise in several temperature cycles. In all cases we found a linear dependence.

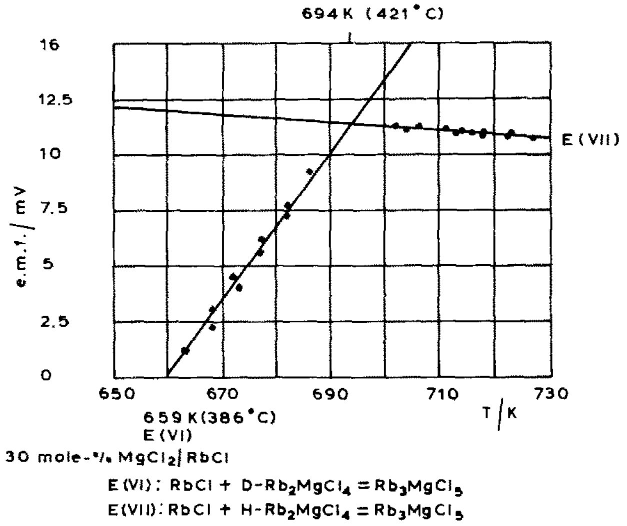

Fig. 4. EMF vs. T-curves for Rb_2MgCl_4

If a phase transition occurs, it must be $\Delta G^r(I)=\Delta G^r(II)$. In fig. 4 an example is given for the transition of D-Rb_2MgCl_4 to H-Rb_2MgCl_4 at 421°C. By DTA temperatures of 443°C (heating curve) and 415°C (cooling curve) were found.

If a compound is formed or decomposed at a certain temperature, like Rb_3LaCl_5 (ref.10). ΔG^r and the E.M.F. must become zero at the temperature of decomposition. However, in a cooling cycle, the compound can be undercooled to a certain degree: we are measuring a negative E.M.F. and a positive ΔG, resp.. This indicates that the compound is existing in a metastable state!

A good impression for the time-dependence of metastability is found from continously measured EMF vs. T-curves. For $RbSrCl_3$, which is existing at temperatures higher than 356°C such a curve is shown in ref. 12. With a cooling/heating rate of 5° per hour one needs 6h for yielding complete decomposition when cooling, and 3h for re-formation when heating.

This is the reason why such compounds can be obtaind metastable at room temperatur be quenching. A good example is Cs_3CdCl_5 ([1]p.90). This congruently meltinc compound is stable at temperatures >395°C. By quenching the melt it can be obtained in a metastable form at room temperature. In DTA heating experiments at ~200°C an exothermic effect is measured the activation energy has become so great that a stable mixture (1 CsCl+1 Cs_2CdCl_4) is formed. Then at 395°C an endothermic effect indicates the "thermodynamically correct" formation of Cs_3CdCl_5. (This reaction can be seen in a dynamic high-temperature X-ray photograph very well). After having annealed the sample at ~300°C for two days, the exotherm could not be found again.

Unfortunately, the reaction time can become so long that the cooling rate of DTA is like quenching. This behaviour was found for $K_{2.08}Ba_{0.96}Cl_4$([1], p.104). In normal cooling and heating experiments the compounds seems to be stable at all temperatures. The formation temperature of 411°C obtaind by EMF-measurement could only be found from DTA-heating-curves at 420°C, after having annealed the compound for some days at ~380°C, near below the formation temperature.

The worst situation exists, if also annealing does not help any longer. An example is $KMnCl_3$ (ref.13). It is a congruently melting compound which crystallizes with the perovskite structure. Two displacive phase transitions occur at 386 and 300°C; at room temperature the perovskite structure is orthorhombically distorted. There is no effect of annealing the compound at temperatures up to 300°C. - However, according to Horowitz et al. (ref.14) the stable room temperature modification is crystallizing with the NH_4CdCl_3-structure. We have prepared this modification by dehydrating $KMnCl_3 \cdot 2H_2O$ at 120°C. The transition temperature to the first high-temperature modification was found by DSC at 267°C.

CONCLUSIONS

DTA measurements are now as ever the most common method for elucidating phase diagrams. They give sufficient results for solid liquid and displacive solid-solid transitions, especially when supported by X-ray photos to determine exactly the composition of

the solid phases. If the enthalpies for the solid transitions become to weak it is profitable to use additional methods which are more sensitive for small alternations of symmetry.
The situation will become much more complicated if reconstructive phase transitions occur. Here it depends on the relation heating (cooling) rate to the reaction time if DTA will give much or more sufficient results or not. If both times are of the same magnitude one will find a hysteresis of temperatures from heating and cooling curves. The equilibrium temperature is lying between both. If the hysteresis is small the DTA temperatures are close to the equilibrium temperatures. (Among the eight ICTA temperature standards only KNO_3,SiO_2, K_2SO_4 and K_2CrO_4 fulfill this requirement.)
If the reaction time is considerably smaller then the time constant of DTA, the reaction no longer can be detected. By more or longer annealing one can try to complete the reaction. If this is successful one will find an effect in heating curves, however at a too high temperature. If the reaction should occur at a temperature where the mobility of the ions in the lattice has become too small, neither annealing will help. Here the only suitable method is to try to prepare the substance at a temperature below the transition point. But what is the matter if the reaction should occur not far from T=0? That is a still open question. Maybe, at this point philosophy begins.

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