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THERMAL ANALYSIS FOR GENERATING PHASE DIAGRAMS OF SYSTEMS ALKALI METAL CHLORIDE/DIVALENT METAL CHLORIDE

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ABSTRACT

After a historical survey of the application of differential thermal analysis (DTA) for the generation of phase diagrams, particularly those of pseudobinary halide systems, the authors' research work on the systems ACl/MCl_2 (A = Na–Cs) is reported. In addition to DTA measurements the thermodynamic properties of the ternary compounds A_nMCl_{n+2} are investigated by solution calorimetry and EMF measurements dependent on temperature with a newly developed galvanic cell for solid electrolytes. This method is also a useful tool for elucidating phase diagrams, especially for reactions occurring in the solid state.

INTRODUCTION

Phase diagrams at constant pressure are representations of one- and two-phase regions with their phase boundaries, if we deal with binary systems, dependent on temperature and concentration. If we assume chemical equilibrium the phase regions are zones of minimal Gibbs energy and the coexistence of phases is governed by the Gibbs phase rule. To generate a phase diagram means to detect all phase boundaries. In general, this is not done by measuring ΔG values in dependence on T (or C), but by measuring heating and cooling curves by DTA. Thus, the enthalpy of phase reactions is utilized, which is related to the free enthalpy, ΔG, by the heat capacity, C.

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. The most effective is 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. But that is not possible in all cases. A further useful method is the application of high-temperature X-ray techniques.

Our own investigations using these techniques, and this review, concern

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the pseudobinary systems ACl/MCl_2 with the limitation that A = Na, K, Rb, Cs and M = alkaline earth metals, Eu^{2+}, light transition metals (Sc–Zn), Cd, Pb; that is, compounds with Li, Tl, for example, and Ge, Sn, Hg are neglected.

We started our work in 1959. At this time maybe one-half of the systems of interest were known through the work of mainly Russian scientists. A good literature compilation up to 1954 is given by N.K. Voskresenskaya in the "Handbook of Solid–Liquid Equilibria in Systems of Anhydrous Inorganic Salts" [1]. The first systematic studies of chloride systems were carried out at the beginning of this century in Italy by Sandonnini, Scarpa et al. and somewhat later in Germany by Vortisch and Korreng. In all these investigations special stress was laid on the study of the solid phases separating out of the melt, and of the transformations in the solid state. In the following period, many workers set themselves the task of preparing definite phases (solid solutions or double salts) with the purpose of studying their structure and clarifying the crystallochemical conditions of their formation (e.g., the studies of Bruni and Ferrari).

In the Soviet Union, an intensified study of anhydrous salt systems began in the 1930s by A.G. Bergmann, with Palkin, Dombrovskaya, Belyaev, and others—all pupils of Kurnakow. The main question studied was the course of exchange reactions in anhydrous systems. The solid phases themselves, their composition, and transformations were studied to a much smaller extent. In most cases the only operation was visual observation of incipient crystallization temperatures. This method cannot be used to determine the composition of incongruently melting compounds; researchers working by visual observation only usually assign to such compounds a composition corresponding to the nearest stoichiometric ratio of the components. Thus, it was not only our task to investigate systems not yet known, but also to reinvestigate a lot of partially known systems with special regard to solid state reactions. This could be done with success only by additional improvement of the research methods.

Thermoanalysis and phase diagrams–a historical survey

Since the discovery of fire the effect of "heat" on various materials was known, but a more quantitative way of applying "heat" was only possible after the development of reliable high temperature thermometers. In about the last hundred years thermocouples, resistance thermometers and optical pyrometers were invented and tested.

Le Châtelier introduced the Pt–Pt/10% Rh thermocouple, up to now the most reliable and chemically stable high temperature thermocouple. For temperature calibration he employed the now common practice of using temperature fixed points; he himself used the boiling temperatures of water and sulphur and the fusion temperatures of selenium and gold. In 1887 [2] he described a heating curve method for the identification of various clays. He used a single thermocouple in the centre of an electrically heated furnace. The output of the thermocouple immersed in the sample is registered photographically by means of a periodically illuminated galvanometer mirror. If an endothermic effect occurs, the spacing of the registered marks is little or zero, "point of arrest", for exothermic reactions the distance becomes bigger.

The first thermal analysis

Four years later Roberts-Austen [3] improved the photographic registration. The photoplate is moved vertically with a constant rate. The vertical motion of the plate then gives the time while the deflection of the galvanometer gives the temperature. With this apparatus called a "recording pyrometer" one gets real temperature–time curves from heating or cooling experiments.

Because Roberts-Austen was interested in alloy research the sensibility of his recording pyrometer had to be increased. This was done by balancing the greater part of the EMF of the thermocouple with an auxiliary measured EMF from a galvanic cell [4]—a differential method!

Unfortunately, the rate of heating or cooling must be absolutely constant otherwise additional effects are created in the sensitive recording system. To avoid these effects from outside the sample, Roberts-Austen balanced the EMF of the thermocouple in the substance under examination with the EMF of a second thermocouple placed in a compensating piece of copper, platinum or fire-clay in the same thermal surroundings [5]. By adding a second sensitive galvanometer to his recording pyrometer he was also able to record ΔT–time curves—the first DTA apparatus with photographic registration had been invented! He used this technique to determine the phase diagrams for carbon steels and hence the properties of railway lines from various sources and manufactured in differing ways (Fig. 1). "It is evident that Roberts-Austen's final photographic apparatus, although very sensitive, was also complicated and very delicate of adjustment and in practice it took

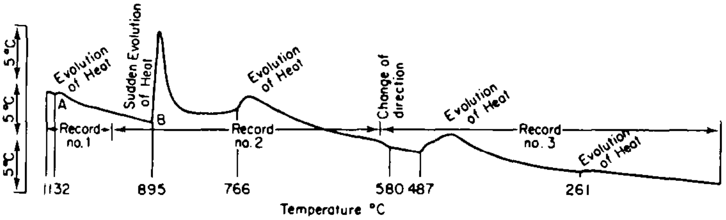


Fig. 1. DTA curve obtained by Roberts-Austen for "electro-iron" with Pt as reference material [4,5].

great skill in its use, requiring for instance some three or four successive exposures adjusted to the proper adjacent temperature ranges, to take the cooling curve of a steel from 1100°C to 200°C" [6].

To avoid the disadvantage of the photographic registration needing an absolutely dark room, galvanometric recorders were described very early (1904), but the recording interval was about 15 s from point to point, much too slow for the detection of rapid and small transformations [6]. In the following decades two methods of registering DTA curves were most commonly used:

(1) observation of the "ΔT-galvanometer" and the temperature-indicating instrument by an observer—very time consuming and tiresome;

(2) the use of a photographic recording system as described by Roberts-Austen [5] or by Salachin in 1903, who invented a method for recording ΔT vs. T on a fixed photoplate using a single light source and two galvanometers! [6].

Up to 1950 in most papers describing the use of DTA for the investigation of various materials, the ΔT curve is not used quantitatively for the determination of enthalpy changes, but as a sensitive indicator of something happening at a certain temperature.

Another very sensitive method for the determination of temperatures of liquidus–solidus lines in a phase diagram is the visual observation of incipient crystallization during continuous stirring and cooling of the melt. This "visual-polythermal method" (a technique used only by Soviet workers starting from the 1930s) did not record DTA curves, but only cooling curves. The recording set-up generally used up to the 1960s was the "Kurnakow Pyrometer", an improved version of the photographic registration apparatus of Roberts-Austen [3,4]. The vertically moving plate is replaced by a rotating cylinder wound with sensitive paper for registration of the deflection of the galvanometer. Five different speeds may be applied to the cylinder, and the apparatus is provided with an EMF compensating system for maintaining maximum sensibility in different temperature ranges. (The most sensitive temperature range is about 250 K for 200 mm registration). The apparatus must be placed in a dark room, but by means of an auxiliary telescope and a red, illuminated scale system the experiment may be controlled from outside [6].

With the investigations of Roberts-Austen and Kurnakow the pioneer time of DTA was finished. Improvements during the next decades mainly concerned problems of miniaturizing samples and raising the accuracy of the equipment. Thus, electronic methods of temperature control and the processing and recording of signals from thermocouples have been of primary interest.

DTA INVESTIGATIONS OF OUR OWN

One of the authors was first involved in DTA during work on a dissertation in the group of Prof. Ehrlich (Inst. Anorg. Chem., Univ. Giessen). Ehrlich [7] had done investigations about the existence of monohalides of the alkaline earth metals, for instance CaCl in the system $Ca/CaCl_2$. He intended to prove by DTA measurements that this compound exists, congruently melting at 50 mol% $CaCl_2$, in contrast to previous investigations of Cubiciotti and Thurmond [8] and Schäfer and Niklas [9]. According to these authors, such sub-halides could not exist.

The error of Ehrlich depended on the material used for his sample containers: he used crucibles of iron which were protected with hydrogen against air corrosion. At high temperatures of ~ 1000°C the hydrogen diffused through the iron and formed calcium hydride, CaH_2. In reality they had investigated the system $CaH_2/CaCl_2$ which contains the congruently melting compound CaHCl. Thus, they had detected a new group of compounds, the alkaline earth hydride chlorides [10] instead of the sub-halides. In argon atmosphere they later on confirmed the results with the real system $Ca/CaCl_2$.

The apparatus of Ehrlich consisted of a home-built furnace, a millivoltmeter as a measuring instrument for temperature, and a galvanometer for the temperature difference. With the same set up Seifert investigated the system ACl/VCl_2 (A = Cs, K, Na) [11] using open nickel crucibles and solved the

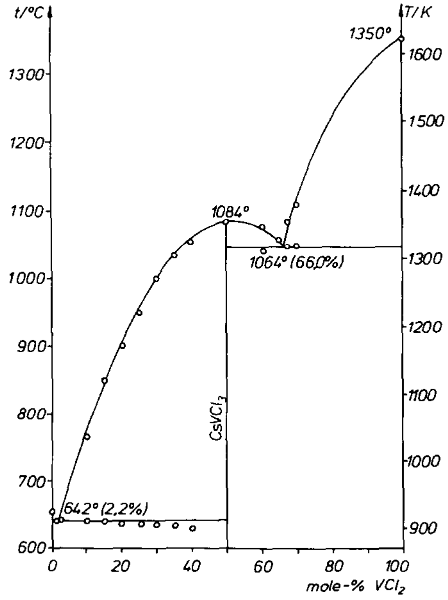


Fig. 2. The system $CsCl/VCl_2$ [11].

structures of the existing compounds. Fortunately, the systems are simple (Fig. 2), so that the results were correct as we could confirm at a later date with a modern apparatus. Difficulties arose with the high volatility of VCl_2 above 800°C. Thus, the melting point was determined with Al_2O_3 crucibles, sealed in iron containers. They were heated to a certain temperature, and after opening they were observed to see if the substance had melted.

The first improvement of the DTA apparatus

In 1960 the visual reading of two needle instruments was substituted by a registration of T and ΔT values with an automatic recorder (Fotocell-Kompensator, Hartmann u. Braun, Frankfurt am Main). This instrument had one handicap: the temperature compensation had to be switched over nearly every hour. It was the first step in our work on improving thermoanalytical units when Dr. Thiel constructed a self-acting changeover switch, utilizing a grilling motor bought in a department store.

During the sixties we mainly investigated systems of divalent chlorides of transition metals, using open quartz crucibles with samples of ~ 2–4 g. The set-up of our apparatus, called "Uschi" is shown in Fig. 3. Applying such large amounts of substance had three advantages: (1) we also had enough substance for X-ray and magnetic measurements; (2) we obtained relatively

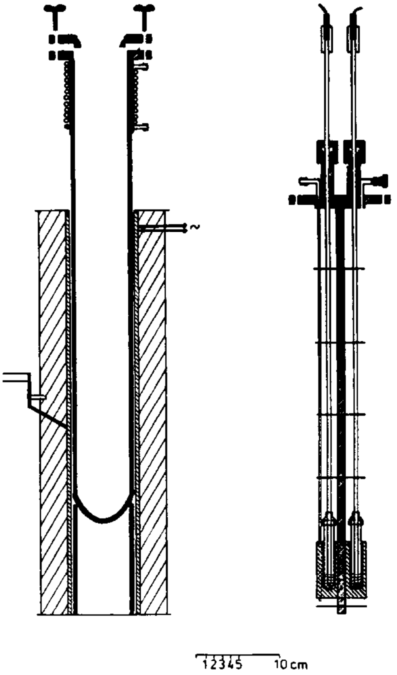


Fig. 3. DTA cell for open crucibles ("Uschi").

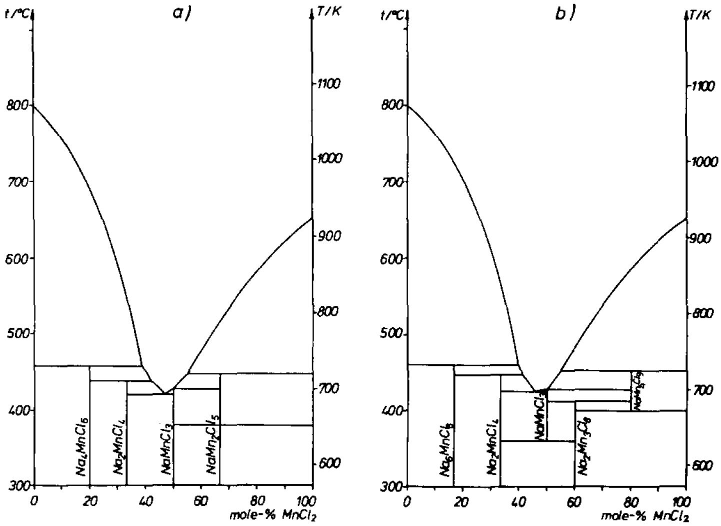


Fig. 4. The system $NaCl/MnCl_2$. (a) First investigation in 1965 [12]; (b) re-investigation in 1977 [13].

good liquid curves from cooling measurements, since after a period of undercooling, the large mass delivered such a great heat of crystallization that the temperature jumped back almost to the correct value; (3) in systems with severe undercooling this could be diminished by stirring the melt with the protection tube of the thermocouple. On the other hand, there was also non-negligible disadvantage caused by the use of such large amounts of substances: during the freezing of the melts sedimentation generally occurred; thus, the solids formed were not homogeneous. The consequence was that eutectics were also found at "the wrong side" of incongruently melting compounds. A typical example is shown in Fig. 4, compared with the later corrected version made with a new, but again home-constructed, DTA cell [12,13].

The present DTA cell

The most helpful improvement was the development of a DTA cell (Fig. 5) for small, sealed quartz ampoules (10 mm diameter, 60 mm length) [14]. Samples of ~ 0.5 g were weighed in a dry box and, after sealing, the ampoules were heated with a gas flame, homogenized by shaking the molten sample and solidified by rapid cooling. The solids thus obtained were sufficiently homogeneous to be used for measuring heating curves or for annealing experiments. Another advantage was that volatile substances, like $NiCl_2$, could be measured without loss of substance. With this apparatus we have succeeded in correcting a lot of phase diagrams during the last ten years. An interesting example is the re-investigation of the system

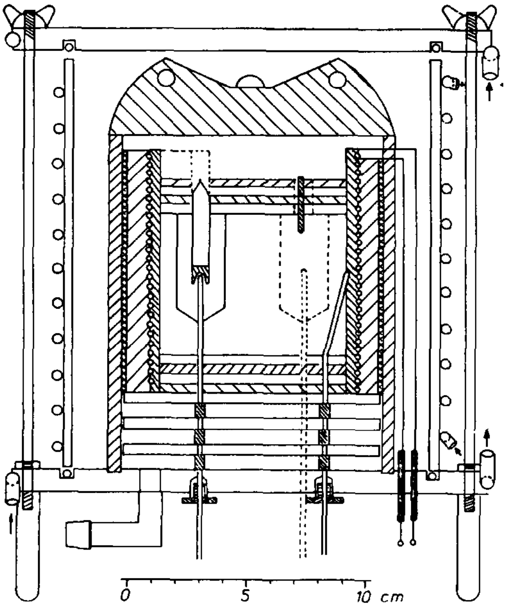


Fig. 5. DTA cell for sealed quartz ampoules [14].

$CsCl/CdCl_2$ performed in 1979 [15]. The contradictory results, taken from the literature, are compiled in Table 1. The main corrections, found by our new DTA measurements and confirmed by X-ray photographs are as follows (Fig. 6).

(1) On the $CdCl_2$-rich side of the system an incongruently melting compound exists instead of a phase transition of $CdCl_2$ at 431°C.

(2) The compound $Cs_3Cd_2Cl_7$ (isostructural with $Rb_3Mn_2Cl_7$) decomposes in the solid state at 450°C.

(3) The congruently melting compound Cs_2CdCl_4 has a transition point at 459°C from the K_2NiF_4-structure type with connected $CdCl_6$-octahedra to the β-K_2SO_4 type with isolated tetrahedra. The transition enthalpy is of the same magnitude as the melting enthalpy. This transition shared between

TABLE 1

Literature on existing compounds (since 1968)

Seifert and Koknat, 1965 [12]					
	Cs_3CdCl_5	Cs_2CdCl_4	$Cs_3Cd_2Cl_7$	$CsCdCl_3$	$CsCd_5Cl_{11}$
From aqueous solution [16]					
		Cs_2CdCl_4	$Cs_3Cd_2Cl_7$	$CsCdCl_3$	
Belyaev et al., 1972 [17]					
	Cs_3CdCl_5	Cs_2CdCl_4		$CsCdCl_3$	
Iskandarov and Ilyasov, 1976 [18]					
Cs_4CdCl_6		Cs_2CdCl_4		$CsCdCl_3$	α- + β-$CdCl_2$

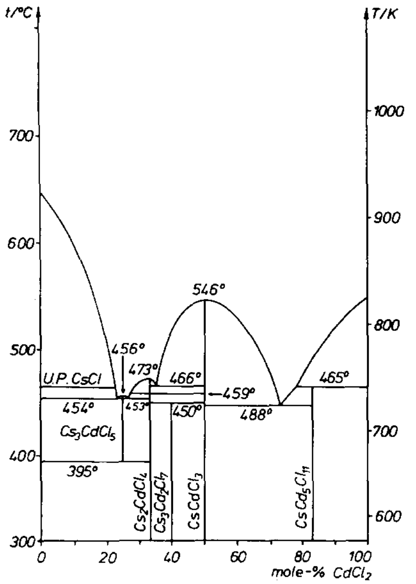


Fig. 6. The system $CsCl/CdCl_2$ [15].

the isolated polyhedra, combined with a volume expansion of about 10%, is somewhat like a premelting effect. Thus, when cooling the melt an undercooling of 14°C occurs and at 459°C the low temperature modification is directly crystallizing.

(4) The congruently melting compound Cs_3CdCl_5 (Cs_3CoCl_5-structure) 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 (Fig. 7): 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 (Fig. 8).) After having annealed the sample at ~ 300°C for two days, the exotherm could not be found again.

Another unusual behaviour was found with the compound $RbCdCl_3$. Crystallized from the melt it has the cubic perovskite structure. At room temperature this structure is deformed to the orthorhombic $GdFeO_3$-type (transition temperature 114°C). But this type is only metastable: during several weeks a stable modification is formed with NH_4CdCl_3-structure. It can be obtained directly by crystallization from aqueous solution. Analogous features were found for $KMnCl_3$ [20]. It is a congruently melting compound which crystallizes with perovskite structure. Two displacive phase transitions occur at 386 and 380°C; at room temperature the structure is distorted, as was found for $RbCdCl_3$. According to Horowitz et al. [21] the stable room temperature modification of $KMnCl_3$, crystallizing with NH_4CdCl_3 struc-

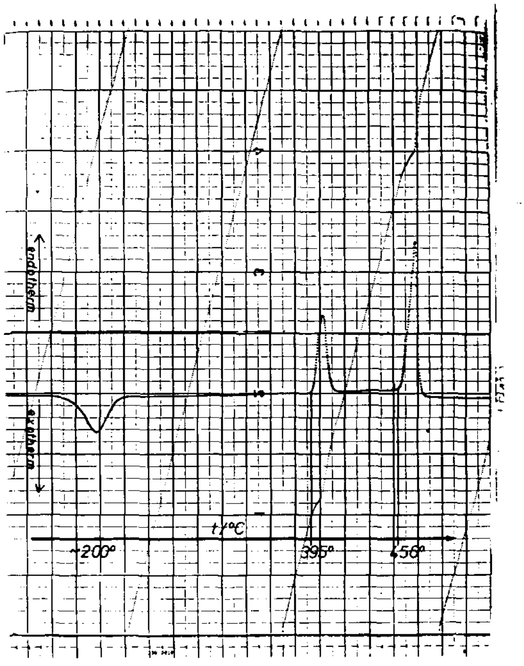


Fig. 7. System $CsCl/CdCl_2$: DTA traces of a quenched sample of Cs_3CdCl_5 (heating curve).

ture, is formed so slowly that it cannot be detected by DTA. The best way of preparing this sample is by the dehydration of $KMnCl_3 \cdot 2H_2O$ at 120°C. (This temperature was found by a thermogravimetric experiment.) To obtain a starting material of correct composition, the dihydrate was prepared by exposing $KMnCl_3$ to ambient air for a few days.

The transition to the high-temperature modification was found by DSC (Prof. Eysel) at 267°C with a transition enthalpy of 4.60 kJ mol^{-1}. However, as described by Horowitz, this temperature can vary between 150 and 270°C, probably due to kinetic effects.

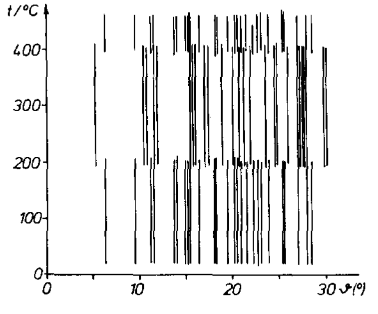


Fig. 8. High-temperature X-ray photograph (Simon–Guinier technique [19]) of a quenched sample of the composition $3CsCl + CdCl_2$.

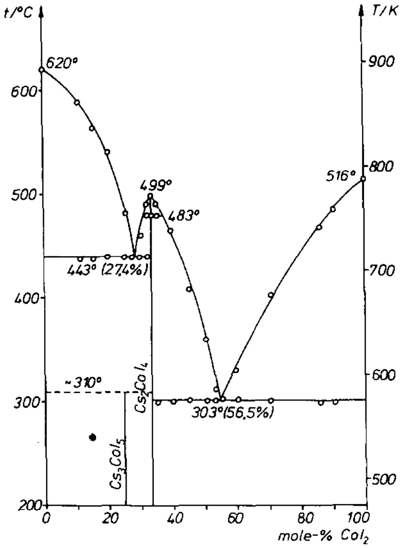


Fig. 9. The system CsI/CoI_2 [22].

A similar limitation of DTA was found when investigating the system CsI/CoI_2 (Fig. 9) [22]. Here the compound Cs_3CoI_5 decomposes on heating to 310°C according to dynamic high-temperature X-ray photographs. The enthalpy of reaction is nearly zero; no DTA effects could be found. The compound can be prepared from aqueous hydroiodic acid as green crystals.

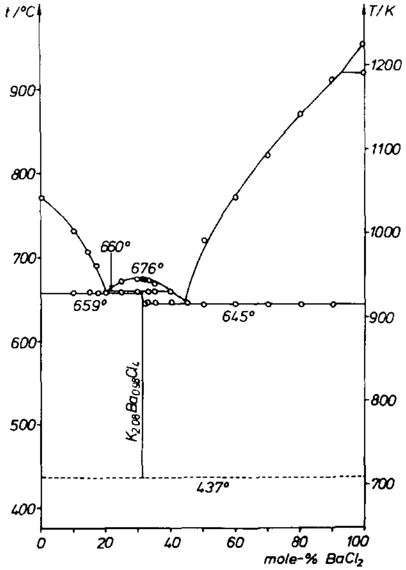


Fig. 10. The system $KCl/BaCl_2$ [23].

Preparation from the melt is not possible. After annealing a sample of the correct stoichiometry for two weeks at 270°C only ~ 20% Cs_3CoI_5 was formed.

Another remarkable result was found on investigating the system $KCl/BaCl_2$ (Fig. 10) [23]. Only one compound exists with an irregular stoichiometry, $K_{2.08}Ba_{0.96}Cl_4$. This was ascertained by careful measurements of the presence of the eutectic at 645°C with high-resolution DTA and additionally by X-ray patterns. Under the normal conditions of DTA measurements no phase transition could be detected. However, after annealing the compound at ~ 380°C for one week it was completely decomposed, and heating curves revealed an endothermic effect at ~ 420°C indicating the re-formation of this high-temperature compound. The melting behaviour is also irregular: a very strong endothermic effect at 660°C is followed by a small shoulder at 676°C. Thus, we have provisionally alleged a region of two non-miscible melts. (It should be pointed out that evidence exists from X-ray patterns that the compound is related to the Th_3P_4-type of structure: in $(K_2Ba)Cl_4$ a substitution of 0.04 Ba^{2+} by 0.08 K^+ has occurred.)

Conclusions

When elucidating phase diagrams by means of DTA measurements one has to take into account two kinds of limitations: one originating from the procedure of measurement and the apparatus, the other being caused by the chemistry of the reaction of interest.

It is a trivial fact that thermal effects with enthalpy changes smaller than the sensitivity of the DTA device cannot be measured. An example of this is the compound Cs_3CoI_5, others well known from the literature are the displacive transitions of perovskites, like $KMnCl_3$. The only safe way to solve this problem is to utilize other methods, like high-temperature X-ray measurements. Other useful methods sometimes applied are the measurement of electrical conductivity, electrical polarisation, magnetic susceptibility, birefrigence, etc.

Another error related to the procedure of measurement is the "wrong stoichiometry" of incongruently melting compounds, which is dependent on the sedimentation effect when a solid of different density separates from a melt. Thus, the solid cannot become homogeneous and when heated again one will find a "wrong eutectic" and thus an incorrect compound composition. A demonstration of this effect is given in Fig. 11. To avoid this behaviour one has to use homogeneous samples which have been annealed just below the peritectic temperature to guarantee chemical equilibrium throughout the whole sample. This can be achieved very simply with our sample holders, in the form of sealed quartz ampoules, in which melts can easily be quenched, as described above. Another advantage is that quartz is generally inert against chloride melts up to ~ 1000°C. Furthermore, we can

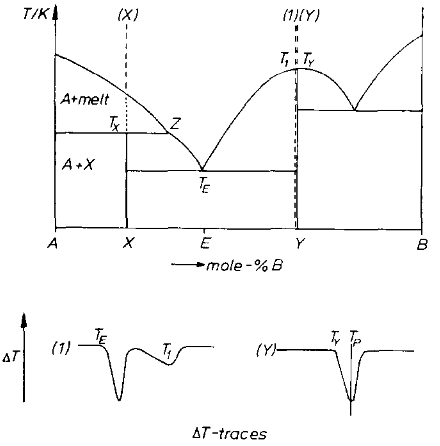


Fig. 11. Binary system with two compounds: X, incongruently melting, Y, congruently melting. When cooling a melt X, at T_X the reaction (A + melt Z) → X occurs. If the reaction is incomplete, the rest of the melt forms (at T_E) a metastable solid E. In the following heating curve an additional eutectic effect is measured at T_E.

use sample sizes of 0.1–0.5 g, which are very convenient when handling strongly hygroscopic compounds, like $CaCl_2$ or $MgCl_2$. The maximum sensitivity and resolution of temperature is achieved with samples of 0.1 g. Because of the poor thermal conductivity in the samples and towards the temperature sensor, we can apply maximum heating rates of only 5 K min^{-1}. Under these conditions the transformation of a mixture of the temperature standards SiO_2 and K_2SO_4 (temperature difference = 10 K) gives two discrete peaks.

The second group of limitations in using DTA measurements for elucidating phase diagrams originates from the kinetics of the reaction of interest. Reconstructive phase transitions and solid state reactions may have such large activation energies that the heating rate of the DTA measurements (generally 1–2 K min^{-1}) is too rapid to allow the reaction to take place at the "correct" temperature. Thus, one will find a large hysteresis between reaction temperatures from heating and cooling curves. In extreme cases we will find no peak in the cooling curve at all; the rate of cooling has the effect of quenching. Examples were given with the α–β transition of Cs_2CdCl_4 and with the compound $K_{2.08}Ba_{0.96}Cl_4$. Such metastable systems obtained by too rapid cooling often give exothermic effects in heating experiments at 200–300°C. At that temperature sufficient activation energy is supplied to the system so that it is forced to convert to "thermodynamic legality". In worse cases this can be achieved by long annealing only. The great question is: was the time of annealing long enough; is the compound really stable? In extreme cases one can find a decision only by determining ΔG values. An example of this procedure is given in the final section of this review.

TABLE 2

Melting temperature of KSr_2Br_5 and adjacent liquidus temperatures from heating curves

			(584°C) (T_P)		
		582°C			
	580°C			581°C	
					580°C
			(576°C) (T_Y)		
			KSr_2Br_5		
mol% $SrBr_2$:	60.0	63.2	66.6	70.2	73.2

A peculiar uncertainty can be found in all DTA work on phase diagrams concerning the melting temperature of a compound in relation to the temperatures of the liquidus curve near that compound (T_Y and T_l, in Fig. 11 for example). As the ΔT traces in Fig. 11 reveal, the "liquidus temperature" T_l is taken from the "peak temperature" of the end of melting in a process; however, the melting temperature of the compound, T_Y, is not taken from the peak maximum, T_P, but correctly from the (extrapolated) onset. This procedure must result in a sinusoidal curve as demonstrated in Table 2. A "normal" maximum of the liquidus curves can only be achieved by taking the too high peak temperature T_P. In other words: all temperatures for a liquidus curve near a compound are too high. This has to be taken into consideration by using such values for thermodynamic calculations. The only idea of the authors for solving this problem is to determine these temperatures from the onset temperatures of peaks in cooling curves, using a sufficiently large sample to avoid undercooling effects.

SOLUTION CALORIMETRY

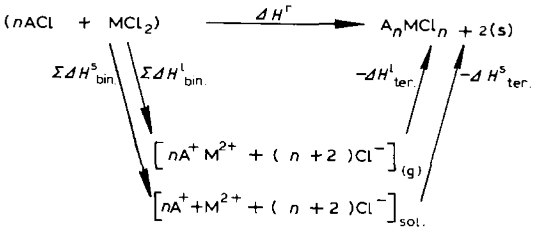
For the reaction of an alkaline metal chloride with the chloride of a divalent metal forming a ternary (or double) chloride, the enthalpy change, ΔH^r, can be expressed as the difference of the lattice enthalpies, as the cycle in Table 3 demonstrates. This difference can be determined by solution calorimetry.

The apparatus used was a home-built isoperibolic calorimeter [24] with a volume of 1.3 l. Samples of 3–6 g thus yielded virtually ideal solutions (dissolution ratio 1 : 3500 mol). The temperature difference between reaction vessel and thermostat was measured with a thermopile; the temperature of the thermostat was constant to 2×10^{-4} K. From the enthalpies of solution, ΔH^s, the reaction enthalpies, ΔH^r, were calculated using the equation:

$$\Delta H^r_{298} = [\Delta H^s_{298}(MCl_2) + n\Delta H^s_{298}(ACl)] - \Delta H^s_{298}(A_nMCl_{n+2})$$

TABLE 3

Enthalpy cycle for the reaction $n\,\mathrm{ACl}_{(s)} + \mathrm{MCl}_{(s)} = \mathrm{A}_n\mathrm{MCl}_{n+2(s)}$



ΔH^{l} = lattice enthalpy; ΔH^{s} = solution enthalpy.

Each ΔH^{s} was measured at least three times; ACl was dissolved in a solution of $\mathrm{MCl_2}$ of suitable concentration. The results for the compounds $\mathrm{AMgCl_3}$ are compiled in Table 4 together with lattice enthalpies, ΔH^{l}, calculated by use of the Born–Haber cycle. There are two main features which need to be discussed:

(1) The highest reaction enthalpies, ΔH^{r}, measured for the compounds $\mathrm{AMCl_3}$ are in the range 30–40 kJ compared with lattice enthalpies of ~ 3000 kJ. The ΔH^{r} values for double chlorides of other compositions ($\mathrm{A}_n\mathrm{MCl}_{n+2}$) are generally still smaller. This situation is comparable with a high plain of 3000 m with small hills and valleys of up to 30 m. It is only a "breath of (lattice) energy" which causes differences in stoichiometry and structure (too small to be calculated by means of approximation models).

(2) If more than one compound exists in the system $\mathrm{ACl/MCl_2}$, each of them must be stable against decomposition into a pair of other compounds, the binary chlorides included. If one assumes that only ΔH^{r}, the difference in lattice enthalpies, is responsible for the stability (an approximation often used in solid state chemistry, which completely neglects entropy changes) then the synproportionation enthalpies, ΔH^{syn}, from the two direct-neighbour compounds must be negative! In Table 5 such values are compiled for the Cs-double chlorides of $\mathrm{Mg^{2+}}$ and $\mathrm{Mn^{2+}}$.

Surprisingly, the values for the compounds $\mathrm{Cs_2MgCl_4}$, $\mathrm{Cs_3MgCl_5}$ and H-$\mathrm{Cs_2MnCl_4}$, all compounds having isolated tetrahedra in their crystal

TABLE 4

Reaction and lattice enthalpies (kJ) of compounds $\mathrm{AMgCl_3}$

	$\Delta H^{\mathrm{s}}_{298}$	$\Delta H^{\mathrm{r}}_{298}$	ΔH^{l}
$\mathrm{CsMgCl_3}$	-108.8 ± 0.3	-29.5 ± 0.4	2974
$\mathrm{RbMgCl_3}$	-115.8 ± 0.3	-23.2 ± 0.4	3083
$\mathrm{KMgCl_3}$	-128.6 ± 0.3	-9.9 ± 0.4	3143
$\mathrm{NaMgCl_3}$	-151.6 ± 0.6	-0.4 ± 0.6	3142

TABLE 5

Synproportionation enthalpies, $\Delta H^{\mathrm{syn}}_{298}$, for caesium double chlorides of Mg^{2+} and Mn^{2+}

Example: $1/2\mathrm{CsMgCl_3} + 1/2\mathrm{Cs_3MgCl_5} = \mathrm{Cs_2MgCl_4}$
$\Delta H^{\mathrm{syn}} = \Delta H^{\mathrm{r}}(\mathrm{Cs_2MgCl_4}) - 1/2\Delta H^{\mathrm{r}}(\mathrm{CsMgCl_3}) - 1/2\Delta H^{\mathrm{r}}(\mathrm{Cs_3MgCl_5})$
$+3.0 = -21.2_8 \qquad +14.7_3 \qquad +9.5_3$

	Cs_3MCl_5	Cs_2MCl_4	$CsMCl_3$	$1/4\ CsM_4Cl_9$
Mg	+2.2	+3.0	−14.9	−2.7
Mn	+12.9	−9.3	−14.8	−1.5
Mn related to high-temperature Cs_2MnCl_4 (K_2SO_4-type)				
	−6.5	+10.1	−28.7	−1.5

lattices, are positive. Thus, these compounds must be either metastable, which seems unlikely, or their stability must originate from a considerable entropy gain, which would give a negative ΔG^{r} at sufficiently high temperature to make the $(T\Delta S)$ term in the Gibbs–Helmholtz equation stronger than ΔH.

THERMAL ANALYSIS WITH A GALVANIC CELL FOR SOLID CHLORIDE ELECTROLYTES

As pointed out in the introduction the free Gibbs enthalpy, ΔG, is the decisive thermodynamic state function for phase diagrams of systems in chemical equilibrium. It is related to the enthalpy, ΔH, by the Gibbs–Helmholtz equation

$$\Delta G = \Delta H - T\Delta S$$

and, as shown in the preceding chapter, compounds exist for which the entropy term, $T\Delta S$, is of predominating importance. Thus, we had to find a convenient way to determine ΔG (and ΔS).

When a reversible galvanic cell can be designed for the process of interest, ΔG can be measured directly electrochemically. The relation to be used is:

$$\Delta G^{\mathrm{r}} = -nFE$$

where n = transported charge, F = Faraday constant, E = EMF. This relation connects the EMF with the Gibbs free enthalpy of reaction, ΔG^{r}, in our investigations with solid state reactions of the type

$$n\mathrm{ACl} + \mathrm{MCl_2} = \mathrm{A}_n\mathrm{MCl}_{n+2}$$

The chemical work released by the formation of ternary chlorides is transformed into electrical energy by our galvanic cell or battery.

If we measure the temperature dependence of the EMF, we also get the entropy of reaction, $-\Delta S^{\mathrm{r}} = (\partial G^{\mathrm{r}}/\partial T)_{p=\mathrm{const.}}$ and, by the Gibbs–Helmholtz-equation, ΔH^{r}. In all our experiments this temperature dependence proved to be linear. Thus, the evaluation could be done by a linear regression analysis: $E = a + bT$, where $a \equiv \Delta H^r$ and $b \equiv -(\Delta S)$. The condition for linearity is

$$\Delta C_p = C_p(A_n\mathrm{MCl}_{n+2})\left[nC_p(\mathrm{ACl}) + C_p(\mathrm{MCl}_2)\right] = 0$$

The idea for these measurements was born at a visit to Trondheim in the laboratory of Prof. Østvold who is working on fused salt mixtures [25]; furthermore, work by Egan [26] experimenting on ACl/$CaCl_2$ cells was stimulating.

THE GALVANIC CELL FOR SOLID ELECTROLYTES [27]

Figure 12 shows the galvanic cell which was used for measuring EMFs associated with the formation of Na_2CdCl_4. A Na^+ ion conducting diaphragm separates a NaCl and $CdCl_2$ disk. In order to obtain a reversible cell we had to use mixtures of $CdCl_2$ with Na_2CdCl_4 instead of pure $CdCl_2$. The anode and cathode are made of graphite disks in chlorine atmospheres. The cell reactions are:

Anode: $2NaCl = Cl_2 + 2Na^+ + 2e^-$

Cathode: $2Na^+ + CdCl_2 + Cl_2 + 2e^- = Na_2CdCl_4$

The sample disks (13 mm diameter; ~ 0.1 g of substance) were prepared by compression with the exclusion of moisture similar to the procedure used in spectroscopy; the separator consisted of compressed Nasicon powder [28] sintered for 15 h at 1375 K. The electrodes (porous graphite) were purified by heating in a chlorine stream at 1075 K for 40 h. Figure 13 shows the whole apparatus: the cell, the wirewound furnace, powered by a temperature-regulated a.c. supply and a d.c. amplifier for the EMF. The output signal was either written with a strip chart recorder or printed digitally in variable time intervals.

Initially the apparatus has heated in a chlorine stream at about 825 K for

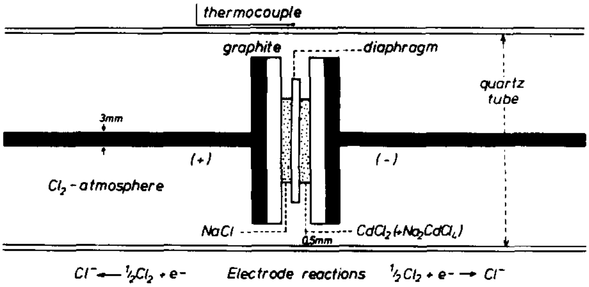


Fig. 12. Galvanic cell for the reaction $2NaCl_{(s)} + CdCl_{2(s)} = Na_2CdCl_{4(s)}$.

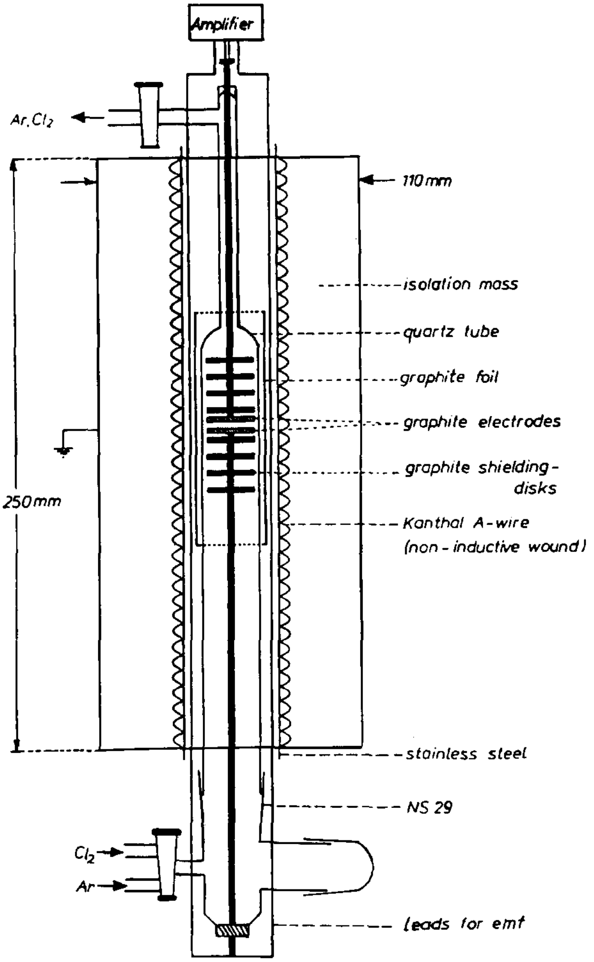
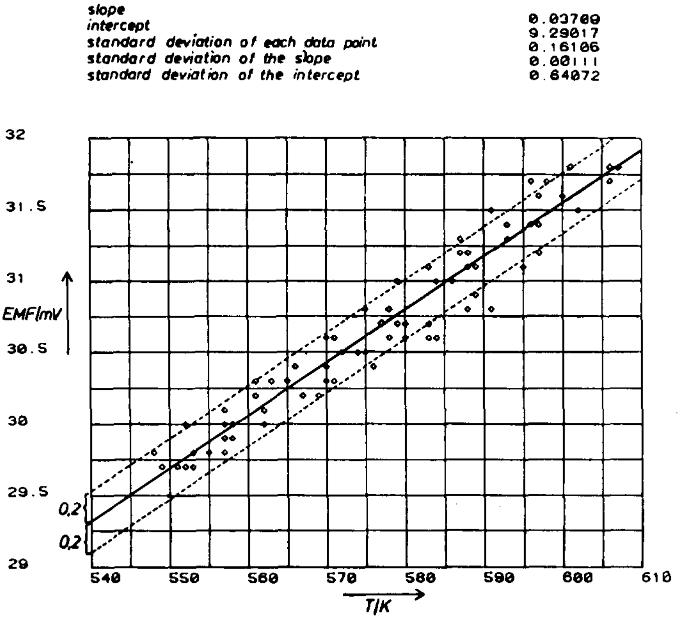


Fig. 13. Cross-section of the set-up for EMF measurements.

one day. Before introduction of the samples the chlorine was replaced by argon. (Chlorine was generated in a Kipp's apparatus from potassium permanganate and concentrated hydrochloric acid and dried with concentrated sulphuric acid and magnesium perchlorate.)

The following procedure of measurements was applied. The graphite electrodes were checked in a $(C + Cl_2)|P|(C + Cl_2)$ cell, where P = NaCl or $CdCl_2$ $(+Na_2CdCl_4)$. In both cases the EMF must be zero, independent of temperature. One electrode was checked with NaCl and one with $CdCl_2$. They were then combined with the sample disks, separated by Nasicon. This "sandwich" was heated to the starting temperature in the measuring set-up and held at this temperature until the EMF remained constant for 4 h. This time could vary between 2 and 20 h. The reversibility of the cell was checked by passing an electrical charge of about 1 mC successively in both direc-



```
slope                                          0.03709
intercept                                      9.29017
standard deviation of each data point          0.16106
standard deviation of the slope                0.00111
standard deviation of the intercept            0.64072
```

Fig. 14. Computer plot of EMF vs. T for the formation of Na_2CdCl_4.

tions. Then the EMF must return to its original value within about 20 min. In this way, the d.c. resistivity of the cell could also be determined. The actual measurement was started. The temperature was changed every 4 h in pre-selected steps. Equilibrium was effectively reached after 0.5–2 h. Two up-and-down cycles were measured.

The upper temperature limit was given by the onset of melting, i.e. the temperature of the lowest melting eutectic. It was assumed that the lower limit was given by the temperature at which the curve of EMF vs. temperature began to deviate from linearity. This temperature is dependent on the particular system: e.g. it was 550 K for $NaCl/CdCl_2$, and 650 K for the system $RbCl/CdCl_2$. For the formation of Na_2CdCl_4 two samples with 50 and 80 mol% $CdCl_2$ were measured. A computer plot of the results from one measurement together with the coefficients of the regression analysis ($E = a + bT$) are given in Fig. 14.

The short-time noise was determined by using an arbitrary sample at an arbitrary temperature with the highest sensitivity. It was found to be ±0.1 mV; i.e. smaller than the uncertainty of the potential follower. The reproducibility of measurements on ten samples of varying composition was ±0.5 mV. Thus the real uncertainty of each measured EMF value is estimated to be not greater than ±1 mV.

The main problem for building such galvanic cells is the use of a suitable diaphragm to prevent a break-down of the EMF by Cl^- conduction. Beside Nasicon for NaCl systems, we have used special glasses with only one alkali metal ion prepared according to a prescription of Østvold [25]. However, such glasses cannot be used for systems of CsCl, because reaction between MCl_2 and caesium silicate occurs. We are currently trying to find diaphragms based on β-alumina.

Thermodynamic functions from EMF values

For the formation of Na_2CdCl_4 the regression equation was transformed to the Gibbs–Helmholtz equation by multiplication with $-2FE(=\Delta G^r)$. Then the mean of both measurements was formed.

$$\Delta G^r(\text{kJ mol}^{-1}) = -1.70 - 0.0073T\ (\text{K})$$

$$\Delta H^r = -1.7 \pm 0.2 \text{ kJ mol}^{-1}$$

$$\Delta S^r = 7.3 \pm 0.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta G^r(578 \text{ K}) = -5.9 \pm 0.2 \text{ kJ mol}^{-1}$$

If more than one compound exists in a system, for instance $AMCl_3$ and A_2MCl_4, we had to do two series of measurements:

(1) For the reaction $ACl + MCl_2 = AMCl_3$ with a cell ACl vs. MCl_2 $(+AMCl_3)$.

(2) For the reaction $ACl + AMCl_3 = A_2MCl_4$ with a cell ACl vs. $AMCl_3$ $(+A_2MCl_4)$.

With a thermodynamic cycle one can also derive the function for the reaction $2ACl + MCl_2 = A_2MCl_4$.

Table 6 gives energy terms for the formation of compounds $AMCl_3$ from ACl and MCl_2 at room temperature. In the chloroperovskites, $RbSrCl_3$ and $RbPbCl_3$ [29], the ionic radii are so unfavourable that these compounds exist only at high temperature by a sufficiently great $(T\Delta S)$ term; or in other

TABLE 6

Energy terms (kJ mol^{-1}) for reactions $ACl + MCl_2 = AMCl_3$ at $T = 298$ K

Compound	ΔG^r	ΔH^r	$-(T\Delta S^r)$	$\Delta H^r_{\text{calorim.}}$
$KMgCl_3$	−13.7	−8.7	−5.0	−9.9
$KCaCl_3$	−15.3	−12.4	−2.9	−15.2
$KMnCl_3$	−16.6	−12.0	−4.6	−15.8
$KCoCl_3$	−11.5	−6.9	−4.6	−7.0
$KNiCl_3$	−10.0	−6.2	−3.8	−8.2
$KCdCl_3$	−19.8	–	−0.6	−19.2
$RbMgCl_3$	−28.9	−27.1	−1.8	−23.2
$RbCaCl_3$	−25.9	−23.1	−2.8	−24.2
$RbSrCl_3$ [a]	−1.0	+5.4	−6.4	+3.6
$RbPbCl_3$ [b]	−3.7	+4.9	−8.6	–

[a] Synproportionation from $0.5RbCl + 0.5RbSr_2Cl_5$: +8.1, +15.5, −7.4, +12.3.

[b] Synproportionation from $0.5RbCl + 0.5RbPb_2Cl_5$: +5.4, +13.9, −8.5, –.

words: they exist from a gain in entropy! (The temperature limit can be calculated from the free enthalpies of synproportionation, also given in Table 6.) Other compounds which also only exist at higher temperatures, where a loss in lattice enthalpy is compensated by a gain in entropy, are K_2CoCl_4 [29], $K_{2.08}Ba_{0.96}Cl_4$ [23], Rb_3MgCl_5 [30] and in systems with trivalent metals, Rb_3LaCl_6 [31]. In all these cases the gain in entropy is caused by the formation of isolated polyhedra (exception: $K_{2.08}Ba_{0.96}Cl_4$), which have additional degrees of freedom for dissipating (thermal) energy. We hope that this thesis can be elaborated to a general rule in solid state chemistry.

EMF measurements for generating phase diagrams

In Fig. 15 a graph is drawn which shows measured ΔG^r values for the formation of double chlorides in the system $RbCl/MgCl_2$ from RbCl and

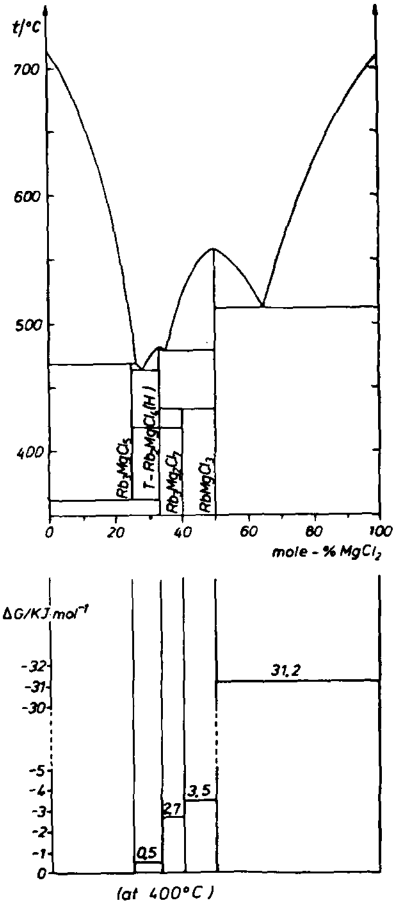


Fig. 15. Measured ΔG^r values in the system $RbCl/MgCl_2$ (400°C).

the $MgCl_2$-rich neighbour compound. This figure reveals two important features:

(1) If a RbCl vs. Rb_3MgCl_5 cell is constructed, or a disk containing less $MgCl_2$ ($MgCl_2$ content, c: $0 < c < 25$ mol%) the measured EMF must be zero, because no additional compound exists.

(2) If we want to measure ΔG^r for the reaction $RbCl + MgCl_2 = RbMgCl_3$, disks with $50.0 < c < 100$ mol% $MgCl_2$ can be used. Going from a composition of 50.1 to 49.9 mol% an abrupt change in EMF is measured. Thus, such measurements can be used for determining the composition of compounds with unusual stoichiometry.

An example of the first situation was found on reinvestigating the system $KCl/NiCl_2$ [32]. By DTA Bolshakov et al. [33] found two compounds: K_2NiCl_4 and $KNiCl_3$, the latter which had a phase transition at 489°C. In contrast to the reported existence of K_2NiCl_4, cells of the type $KCl/(KNiCl_3 + K_2NiCl_4)$ gave EMFs of zero at each temperature, whereas cells with more than 50 mol% $NiCl_2$ as catholyte gave EMFs of about 120 mV (above a temperature limit of 390°C). No break in the EMF vs. T curve was observed at 489°C. DTA and high-temperature X-ray measurements confirmed these results. Recently scientists from the U.S.S.R. obtained the same result [34].

An example of case 2 was found in the system $NaCl/CdCl_2$ (Fig. 16 [32]). There had been considerable difficulty in determining the compositions of the two $CdCl_2$-rich compounds, because they are formed in a peritectic reaction from the melt and are stable only at higher temperatures. The application of EMF measurements for solving this problem will be described for $Na_{10}Cd_{13}Cl_{36}$ (56.2 mol% $CdCl_2$). Figure 17 shows two EMF vs. T

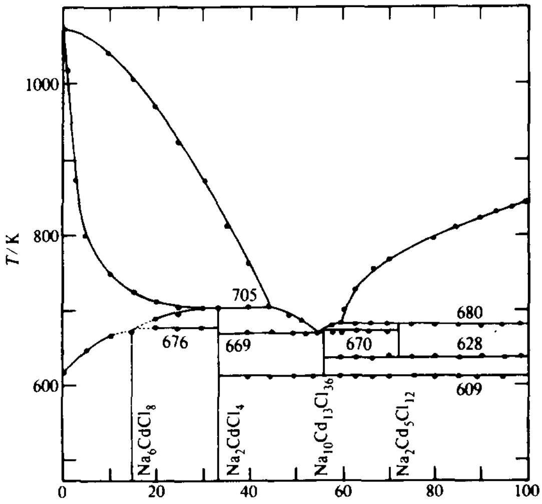


Fig. 16. The system $NaCl/CdCl_2$ [32].

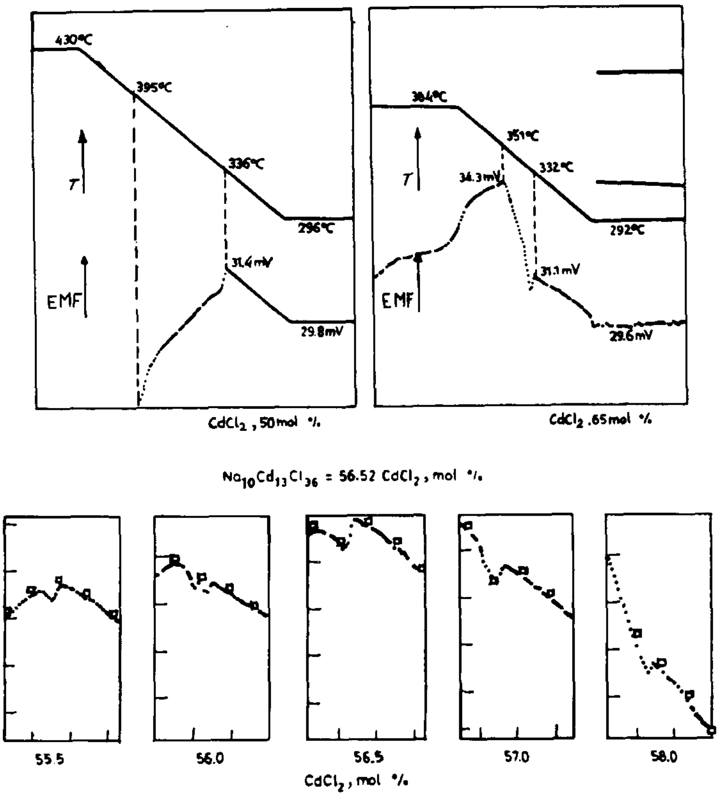
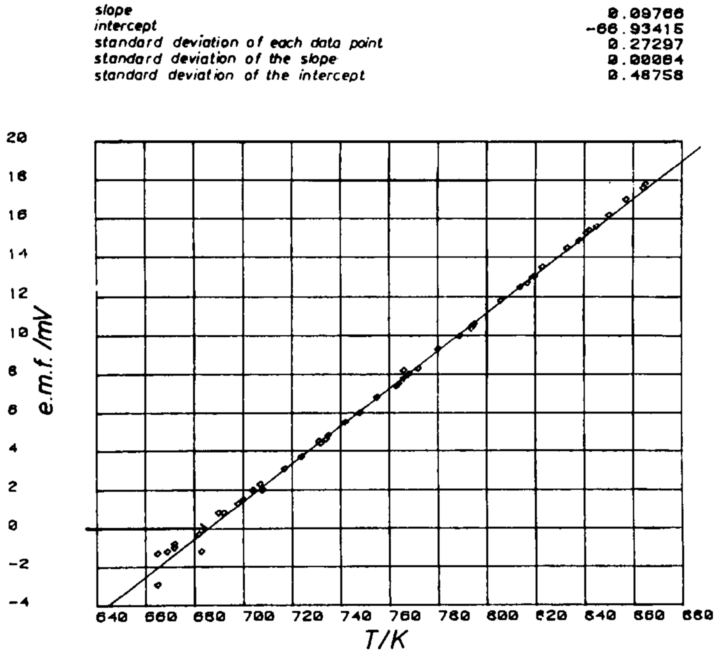


Fig. 17. Continuously measured EMF vs. T curves near $Na_{10}Cd_{13}Cl_{36}$ in the region of 336°C [32].

curves, the left-hand one characteristic for the combination of NaCl disks with disks of composition between 33.33 and 56.52 mol% $CdCl_2$, the right-hand one for $> 56.52\%$. The most obvious difference is the change in slope at 332/336°C. Several measurements on samples with an increasing content of $CdCl_2$ gave curves of the type shown in the second row. The characteristic change in slope occurs between 56.5 and 57.0 mol% $CdCl_2$. The formula $Na_{10}Cd_{13}Cl_{36}$ was derived from EMF 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 $Na_{10}Cd_{13}\square Cl_{36}$.

EMF measurements and "thermodynamic temperatures" for solid state reactions

We saw in one of the preceding sections that the compound $K_{2.08}Ba_{0.96}Cl_4$ does not decompose when cooled below ~ 400°C, the lower temperature



```
slope                                          0.09766
intercept                                    -66.93415
standard deviation of each data point          0.27297
standard deviation of the slope                0.00084
standard deviation of the intercept            0.48758
```

Fig. 18. Computer plot of EMF vs. *T* for the formation of $K_{2.08}Ba_{0.96}Cl_4$ [23].

limit for its stability [23]. Thus, it is in a metastable state at room temperature. (After annealing at ~ 380°C the temperature of reformation was found to be ~ 420°C in a heating curve.) With such an annealed sample (Fig. 18) we measured an EMF of zero at temperatures lower than 411°C (684 K). Above this temperature positive EMFs were found which yield negative ΔG^r values. When cooling the cell below this temperature negative EMFs were found: we had now obtained a metastable system with positive ΔG values; the direction of the reaction had turned to decomposition! Thus, EMF measurements can be a probe for detecting metastable states.

In our example the (regression) analysis of the measured values gave the equation: ΔG^r (kJ mol^{-1}) $= 13.2 - 0.0193T$ (K). The decomposition temperature ($\Delta G^r = 0$) is calculated to be 684 K (411°C). This value is lower than the 420°C value we obtained from DTA heating curves. Another example of differing temperatures was found in the system $RbCl/MgCl_2$ [35] for the transition of the low-temperature modification of Rb_2MgCl_4, crystallizing in the K_2NiF_4-structure with connected octahedra, to the high-temperature form with isolated tetrahedra. We found the temperatures 443°C from DTA heating curves, and 415°C from cooling curves. The hysteresis is 28°C. EMF measurements yielded 428°C.

Both solid state reactions are of the reconstructive type: during transition (or reaction) the ions must be shifted over long distances. It is reasonable that the large activation energies needed are the cause of such large tempera-

	I	II
slope	0,09361	0.06594
intercept	- 18.20326	-0.06922
standard deviation of each data point	0.23713	0.10611
standard deviation of the slope	0,00372	0.00114
standard deviation of the intercept	2.35148	0.78416

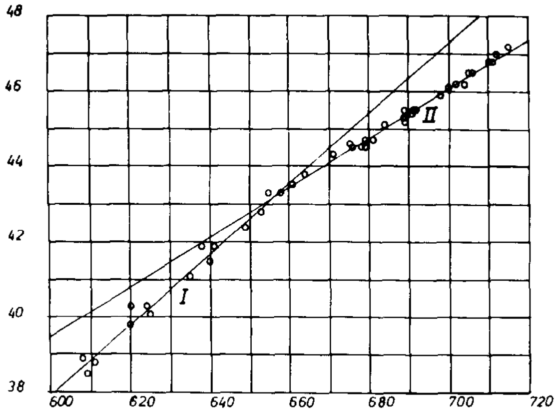


Fig. 19. Computer plot of EMF vs. T for the reaction $0.33KCl + KMnCl_3 = K_{1.33}MnCl_{3.33}$. I, Tetragonal $KMnCl_3$; II, cubic $KMnCl_3$ [20].

ture differences. Reactions of this type should not be used for temperature standards! The displacive phase transition of $KMnCl_3$ from the tetragonal to the cubic perovskite structure gave, by EMF measurements, a temperature of 655 K (382°C) (Fig. 19) [20] compared with 659 K (and 655 K) from DTA measurements. Here the temperature hysteresis is much smaller.

Conclusions and view to the future

The main advantage of this new thermal analysis (TA) method is, that the EMF is an intensive quantity and not an extensive one, like 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 required, and overheating can easily be avoided. Of most practical interest is, in our opinion, its application for detecting metastable states, that cannot be done with any other TA method. A second important use lies in the determination of "correct thermodynamic" temperatures. Temperatures of solid state transitions and reactions determined with dynamic methods (DTA) can differ significantly from the equilibrium temperatures in the case of reconstructive phase transitions. An indication for such deviations is the hysteresis of temperatures from heating and cooling curves. 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.) The main disadvantages are the temperature limitations and the fact that the measurements are limited to solid state reactions.

What is to be done in the near future? Primarily we have to find Cs^+-conducting diaphragms, presumably on ceramic bases. This is of special importance, because the systems $CsCl/MCl_2$ are those containing the greatest number of compounds, a lot of them with isolated $[MCl_4]^{2-}$ tetrahedra. Furthermore, it would be of interest to construct cells with non-oxidating atmospheres. First successful experiments have been performed in an HCl/H_2 atmosphere, and then we will try to transfer our measurements to bromide systems, working in a Br_2 atmosphere.

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