# DIFFERE⸱⸱ AL THERMAL ANALYSIS EQUIPMENT FOR THE STUDY OF MOLT ⸱ FLUORIDE EQUILIBRIA

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ABSTRACT

Equipment constructed for phase investigations by differential thermal analysis (DTA) is described. The samples, usually 1.5–2.5 g, are in platinum crucibles mounted in a nickel block inside a Kanthal-wired "thermal gradient free" laboratory furnace. The reference material is fired $Al_2O_3$. The temperature and the differential temperature are measured by Pt/Pt 10% Rh thermocouples. The differential thermocouple is immersed directly in the molten salt.

The equipment has proved very well suited for phase investigations in molten and solid fluorides, including the detection of solidus curves in systems with solid solubility. A survey of the systems investigated is given.

The equipment has also been tried for quantitative measurements. The enthalpies of fusion of the alkali metal cryolites, $M_3AlF_6$, were measured by DTA, and the results are compared with values obtained by calorimetry.
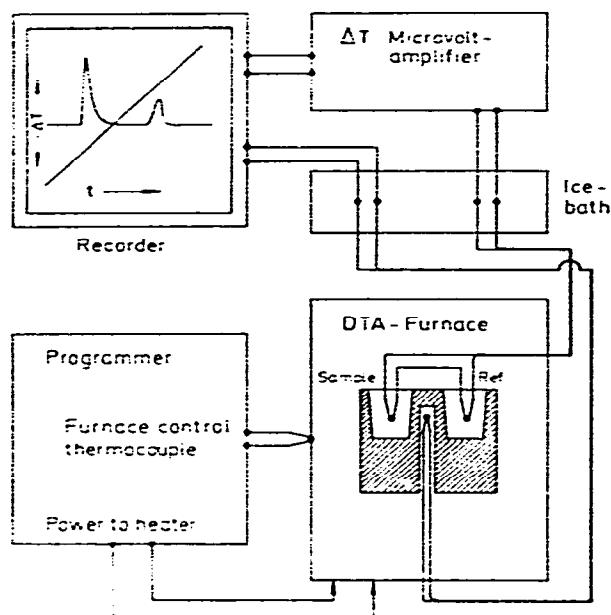
Fig. 1. Schematic diagram of the DTA apparatus.

INTRODUCTION

One of the main research programs at the Institute of Inorganic Chemistry over a number of years has been the study of phase diagrams, especially those related to the electrolytic production of aluminium and magnesium. For this work an apparatus for differential thermal analysis (DTA) was constructed, and has proved very successful. DTA has the advantage over ordinary thermal analysis that the sensitivity is much greater, thus enabling one to work with far smaller samples. DTA is also better suited for the study of solid state reactions than is thermal analysis. An added advantage of DTA over thermal analysis is that DTA is so much faster.

A block diagram of the DTA equipment is given in Fig. 1. In the following the equipment is described in detail. and a survey of the systems investigated by the present authors and co-workers is given.

EXPERIMENTAL

*Furnace unit*

The furnace is a Kanthal A-wired vertical laboratory furnace. The inner tube, made from Pythagoras tubing. has an i.d. of 60 mm and is 45 cm long. The tube is insulated by a layer of diatomaceous earth. and the outer mantle is a water-cooled
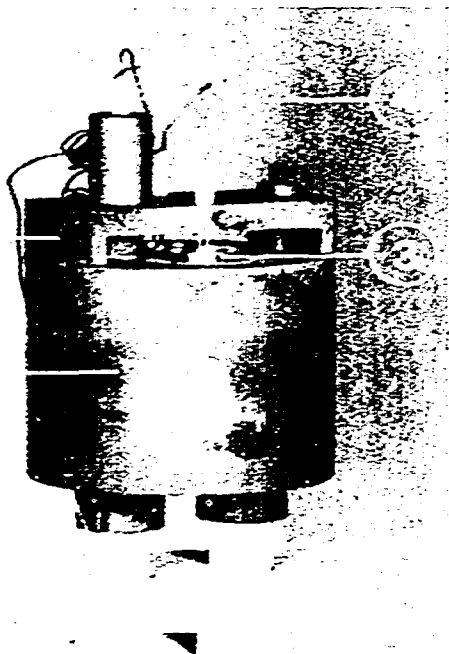


Fig. 2. DTA equipment: 1 = Nickel block, 2 = Nickel cover, 3 = Platinum crucible, 4 = Pt/Pt10%Rh/ Pt thermocouple for recording temperature differences. 5 = Alumina protection tube with Pt/Pt10%Rh thermocouple for recording temperature, 6 = Alundum radiation shields.

copper shield. The tube's ends are closed by water-cooled nickel lids. The power supply is regulated by a variable transformer. In order to reduce the thermal gradient over the length of the furnace, two variable resistances are connected in parallel to the top and middle part of the heater windings. The thermal gradient was found to be less than 0.1 °C/cm over the middle part of the furnace. The nickel block will reduce the gradient in the system still more.

The sample and reference materials are in conical platinum crucibles, top diameter 12 mm, bottom diameter 10 mm, height 15 mm. The crucibles are mounted symmetrically in a nickel block, 50 mm in diameter and 40 mm high. The block and crucibles are covered by a nickel lid. The block and lid are both grounded. This set-up is shown in Fig. 2.

Radiation shields made from alundum cement are mounted in the furnace tube above and below the nickel block.

The temperature is measured by a Pt/Pt 10% Rh thermocouple mounted in a bore in the nickel block. The differential temperature is measured by a Pt 10% Rh/ Pt/Pt 10% Rh thermocouple with the junctions immersed *directly* in the sample and reference material, to obtain the highest sensitivity and least possible time delay. The thermocouples are protected from contact with the nickel block and lid by alumina tubes. The cold junctions are immersed in mercury-filled glass tubes inside a thermos bottle filled with ice and distilled water.

All experiments were carried out in an atmosphere of highly purified nitrogen (99.95% $N_2$, Norsk Hydro A/S, Norway).

*Recording equipment*

The differential signal is amplified by means of a d.c. Microvolt Amplifier, range 50–2000 $\mu$V (Leeds & Northrup Company, Philadelphia). This amplified signal is fed to the recorder, together with the temperature signal. Two different recorders were used, one Speedomax G XY-recorder (Leeds & Northrup Company, Philadelphia) and one Varian G2022 Dual Channel Recorder (Varian Associates, California).

When the XY-recorder was used, the exact reaction temperatures were measured by a potentiometer with an accuracy of ±1 degree. With the dual channel recorder the reaction temperatures were read directly from the curves with the same accuracy, ±1 degree.

In addition to the greater accuracy in temperature readings, the dual channel recorder, where the differential temperature is plotted versus time, has the advantage of being better suited for quantitative measurements than the XY-recorder.

*Chemicals*

The following chemicals were used for the quantitative measurements:

NaCl, KCl, and $Na_2SO_4$ (all p.a. E.G. Merck AG, Germany) were dried in air at 150°C.

LiF (Certified Reagent, Fisher Scientific Company, USA), NaF (p.a. E.G. Merck AG, Germany), KF (anhydrous, granular, min. 99%, Baker & Adamson,

USA), RbF (Grade 2N8+ (min. 99.8%), Koch-Light Laboratories, England), and CsF (Laboratory Reagent (min. 98%), The British Drug House Ltd., England), were all dried in vacuum at 400–450 °C. They were then melted in a nitrogen atmosphere, and clear crystals were selected from the samples.

AlF₃ (technical grade, Riedel de Haën AG, Germany) was purified by repeated sublimation, and clear hexagonal crystals were selected from the samples.

TABLE I

COMPOUNDS STUDIED BY DTA

| Compound | Reference | Observed heat effects due to | |
|---|---|---|---|
| | | Phase transition | Melting |
| $Li_3AlF_6$ | 1, 2 | × | × |
| $K_3AlF_6$ | 3 | × | × |
| $Rb_3AlF_6$ | 3 | × | × |
| $Cs_3AlF_6$ | 3 | × | × |
| $KMgCl_3$ | 4 | | × |
| $K_2MgCl_4$ | 4 | | × |

TABLE II

SYSTEMS STUDIED BY DTA

| System | Reference | Observed heat effects due to | | | | |
|---|---|---|---|---|---|---|
| | | Formation of solid solution | Phase transition | Peritectic reaction | Eutectic reaction | Liquidus reaction |
| $NaCl–KCl$ | 5 | × | | | | × |
| $MgCl_2–CaCl_2$ | 6 | × | | | × | × |
| $NaCl–KCl–MgCl_2–CaCl_2$ | 4 | | | | × | × |
| $NaF–LiF$ | 7 | × | | | × | × |
| $NaF–KF$ | 7 | × | | | × | × |
| $NaF–RbF$ | 7 | | | | × | × |
| $LiF–AlF_3$ | 8, 9, 10 | | × | × | × | × |
| $KF–AlF_3$ | 8 | | × | × | × | × |
| $CaF_2–AlF_3$ | 11 | | × | × | × | × |
| $SrF_2–AlF_3$ | 12 | | × | × | × | |
| $BaF_2–AlF_3$ | 13 | | × | × | × | × |
| $PbF_2–AlF_3$ | 12 | × | × | × | × | × |
| $CaF_2–Na_3AlF_6$ | 14 | | × | | × | × |
| $CaF_2–NaF–Na_3AlF_6$ | 14 | | | | × | |
| $LiF–Na_3AlF_6$ | 9, 10 | × | × | | × | × |
| $Li_3AlF_6–Na_3AlF_6$ | 5 | × | × | | | × |
| $LiF–NaF–Na_3AlF_6$ | 9, 10 | | × | | × | |
| $LiF–Li_3AlF_6–Na_3AlF_6$ | 9, 10 | | × | | × | |
| $Li_3AlF_6–K_3AlF_6$ | 15 | | × | × | × | × |
| $Li_3AlF_6–Rb_3AlF_6$ | 15 | | × | × | × | × |
| $Na_3AlF_6–K_3AlF_6$ | 16 | × | | | × | |
| $Na_3AlF_6–Rb_3AlF_6$ | 16 | × | × | | × | × |

Na$_3$AlF$_6$ was natural hand-picked crystals from Ivigtut, Greenland. The other cryolites were made by fusing alkali fluoride and AlF$_3$ in molar proportions 3:1, in an atmosphere of purified nitrogen.
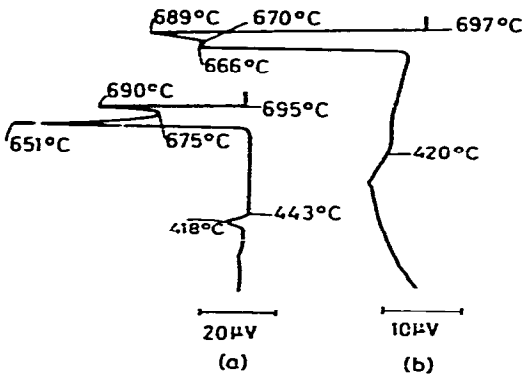
Fig. 3. DTA cooling curves for the system NaCl–KCl. Differential temperature versus temperature: (a) 33.4 mol% KCl, liquidus point 695°C, solidus point 675°C, critical mixing point 443°C; (b) 70.2 mol% KCl, liquidus point 697°C, solidus point 670 C, critical mixing point 420 C.
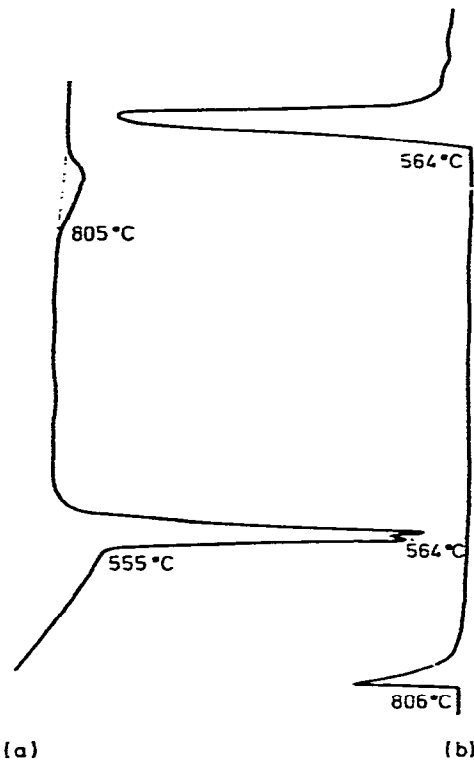
Fig. 4. DTA heating curve (a) and cooling curve (b) for a sample of composition 97.2 mol% Na$_3$AlF$_6$ + 2.8 mol% LiF, versus time, showing the phase transition $\alpha \rightleftarrows \beta$-Na$_3$AlF$_6$(ss) at 555°C and 564°C, respectively, and the reaction NaF(ss) + Na$_3$AlF$_6$(ss) $\rightleftarrows$ liq + Na$_3$AlF$_6$(ss) at 806°C.

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RESULTS AND DISCUSSION

*Qualitative investigations*

In Tables I and II is given a survey of the compounds and systems studied, and the types of reaction which could be detected by means of the equipment. described in the present work.

This DTA set-up has proved very well suited for phase investigations. Of special interest is the possibility to detect small amounts of solid solution.

In Figs. 3 and 4 are given typical curves from systems showing so'id solubility. It is seen that although the enthalpy changes associated with the formation of solid solutions are small. they can be detected clearly by means of the present equipment and techniques.

*Quantitative measurements*

The basic equation relating the peak area to the heat of reaction is

$$\Delta H = k_r \int_1^2 \Delta T dt$$

Here $\Delta H$ is the heat of reaction.

$k_r$ is an aperture constant,

$\Delta T$ is the differential temperature, and $t$ is the time.

1 and 2 signify the beginning and end of the peak.

This equation shows that for quantitative measurements the differential temperature should always be plotted versus the time, and not versus the temperature. If a plot versus temperature is used, much more extensive calibrations become necessary. Although this fact has been known in literature for several years, many authors have apparently not been aware of it. This has led to much confusion, especially when it comes to the question of whether the peak area is dependent on the heating (cooling) rate or not.

The equipment was calibrated by using the melting reactions of the following salts: KCl, NaCl, $Na_2SO_4$. and NaF. The heating rate was 4.05–4.35°C/min, and the cooling rate 2.6–3.5°C/min. Each sample was heated 2–4 times (usually 3) and cooled 1–3 times (usually 2). The results from the first heating, which started with the sample as a loosely packed powder, were always disregarded, and are not given here. These values tended to be much larger than the others.

For the salts used for calibration, the peak area was determined in the usual manner, as shown in Fig. 5a. The actual peak areas were measured with a planimeter. The results of the calibration are given in Table III. The calibration factor $k$ (in cal/area unit) could be expressed as a function of the absolute temperature, $T$:

Heating: $k = -12.832 + 22.781 \cdot 10^{-3} T - 8.333 \cdot 10^{-6} T^2$ (2)

Cooling: $k = -13.940 + 22.940 \cdot 10^{-3} T - 8.542 \cdot 10^{-6} T^2$ (3)

TABLE III

CALIBRATION FACTORS FOR ENTHALPY OF FUSION MEASUREMENTS,
WITH ESTIMATED UNCERTAINTIES

| Compound | Melting (°C) | $\Delta H_f$ (kcal/mol) | Sample weight (g) | Calibrating factor (cal/area unit) | |
|---|---|---|---|---|---|
| | | | | Heating | Cooling |
| KCl | 771 | 6.28[17] | 1.5903 | 1.90 | 1.33 |
| | | | | 1.79 | 1.24 |
| | | | 1.4980 | 1.83 | 1.23 |
| | | | | 1.86 | 1.24 |
| | | | | Mean: 1.85±0.05 | 1.26±0.05 |
| NaCl | 801 | 6.73[17] | 1.5496 | 2.11 | 1.51 |
| | | | | 2.06 | 1.61 |
| | | | 1.7306 | 2.01 | 1.47 |
| | | | | 2.15 | |
| | | | 1.7013 | 1.98 | 1.39 |
| | | | | 1.99 | 1.42 |
| | | | | Mean: 2.05±0.05 | 1.48±0.1 |
| Na₂SO₄ | 882 | 5.67[18] | 1.8955 | 2.42 | 1.81 |
| | | | | 2.31 | 1.78 |
| | | | | (2.62) | 1.85 |
| | | | 2.0045 | 2.30 | 1.65 |
| | | | | 2.39 | 1.63 |
| | | | | 2.34 | 1.65 |
| | | | | Mean: 2.35±0.05 | 1.73±0.1 |
| NaF | 996 | 7.99[19] | 1.0417 | 2.98 | 2.15 |
| | | | 0.9627 | 2.33 | 1.75 |
| | | | | 2.72 | 1.97 |
| | | | 2.0940 | 2.68 | 2.00 |
| | | | | 2.68 | 2.04 |
| | | | 2.2974 | 2.67 | 2.18 |
| | | | | 2.54 | 1.95 |
| | | | | Mean: 2.66±0.1 | 2.01±0.1 |

These equations were calculated by a least squares treatment. The two calibration curves are shown in Fig. 6, together with the mean values of $k$ for each of the salts.

The enthalpy of fusion of the alkali metal cryolites were measured in the same manner. Here the peak area determination was somewhat different. With the exception of $Li_3AlF_6$ all these compounds show strong tendencies to pre-melting, and the usual method of peak determination, as shown in Fig. 5a, gave rather high values for the enthalpy of fusion. The peak areas for these compounds were therefore determined in the manner shown in Figs. 5b and 5c. The results obtained are given in Table IV, together with values from calorimetric work.

As can be seen, the DTA measurements gave values in good agreement with

TABLE IV
ENTHALPIES OF FUSION OF THE ALKALI METAL CRYOLITES, $M_3AlF_6$, BY DTA, WITH ESTIMATED UNCERTAINTIES

| Compound | Melting point (°C) | Sample weight (g) | Enthalpy of fusion (kcal/mol) | | $\Delta H_f$ (this work) | $\Delta H_f$ (calorimetric) |
|---|---|---|---|---|---|---|
| | | | Heating | Cooling | | |
| $Li_3AlF_6$ | 785 | 1.2421 | 22.4 | 19.6[a] | | |
| | | | 21.6 | 18.2[a] | | |
| | | 2.0672 | 19.7 | 16.1[a] | | |
| | | | 19.3 | 16.1[a] | | |
| | | | Mean: 20.8±1.5 | (17.5) | 20.8±1.5 | 21.0[19], 21.5[20-21] |
| $Na_3AlF_6$ | 1011 | 2.1114 | 23.1 | 26.8 | | |
| | | | 24.5 | 27.2 | | |
| | | 2.3535 | 21.4 | 24.2 | | |
| | | | 25.8 | 28.0 | | |
| | | | 24.7 | 24.9 | | |
| | | 2.2100 | 25.9 | 29.2 | | |
| | | | 24.3 | 27.4 | | |
| | | | Mean: 24.2±1.5 | 26.8±2.0 | 25.5±2.5 | 27.91[12], 27.64[23], 27.1[19] |
| $K_3AlF_6$ | 1000 | 1.8636 | 32.3 | 35.2 | | |
| | | | 30.1 | 35.2 | | |
| | | 1.7431 | 27.3 | 31.4 | | |
| | | | 28.2 | 35.5 | | |

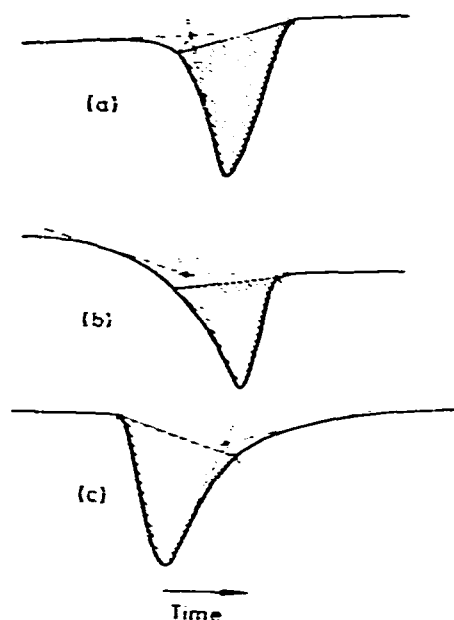| | | | | | | |
|---|---|---|---|---|---|---|
| | | 2.1327 | 34.7 | 36.2 | | |
| | | 2.1000 | 34.1 | 36.4 | | |
| | | | 34.9 | 37.1 | | |
| | | | 33.4 | 34.7 | | |
| | | | Mean: 31.9±3.0 | 35.2±2.0 | 33.5±4.0 | 29.3[19] |
| Rb$_3$AlF$_6$ | 927 | 2.4254 | 36.6 | 32.7 | | |
| | | 2.6674 | 35.6 | 30.9 | | |
| | | | 34.9 | 33.2 | | |
| | | 2.6274 | 36.1 | 31.6 | | |
| | | | 32.2 | 35.3 | | |
| | | 2.8341 | 32.3 | 37.3 | | |
| | | | 35.2 | 38.2 | | |
| | | | 33.7 | 36.7 | | |
| | | | Mean: 34.6±1.5 | 34.5±3.0 | 34.5±3.0 | 31.5[19] |
| Cs$_3$AlF$_6$ | 811 | 2.3549 | 26.8 | 30.1 | | |
| | | 2.8820 | 28.2 | 32.0 | | |
| | | | 31.5 | 34.2 | | |
| | | 2.5967 | 32.3 | 33.8 | | |
| | | | 26.6 | 31.1 | | |
| | | 3.1055 | 26.4 | 28.8 | | |
| | | | 26.8 | 30.1 | | |
| | | 3.1415 | 25.5 | 30.1 | | |
| | | | 30.7 | 31.3 | | |
| | | | 29.8 | 32.5 | | |
| | | | Mean: 28.5±2.5 | 31.4±2.0 | 29.9±2.5 | 29.3[19] |

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Fig. 5. Peak area connected with the melting reaction of (a) compound showing no pre-melting reaction, (b) compound showing pre-melting reaction, heating curve, and (c) compound showing premelting reaction, cooling curve.
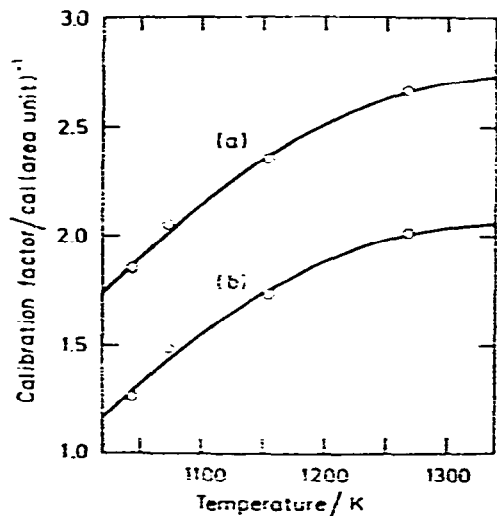


Fig. 6. Experimental calibration factor for enthalpy measurements from (a) heating curves, (b) cooling curves. ○ Mean calibration factors from the compounds KCl, NaCl, Na$_2$SO$_4$, and NaF.

calorimetry for some compounds, while others differ by as much as 15%, or up to 30% for single measurements. We believe the main reason for this variation to be the difficulty in evaluating the peak area correctly when pre-melting occurs. The results show, however, that for compounds without pre-melting, reasonably accurate enthalpy values can be obtained by use of the DTA equipment described here.

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