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DTA AS A METHOD OF STUDYING CHEMICAL REACTIONS AT HIGH PRESSURES

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ABSTRACT

It is proposed that DTA should be used to study chemical reactions under high pressures "in situ". Two techniques are described which allow the investigation of systems including substances of high chemical activity in different pressure ranges. DTA and quantitative DTA under pressure are shown to allow the determination of the reaction products "in situ", as well as the observation of heat evolution during the course of the process.

INTRODUCTION

Differential thermal analysis (DTA), with a history of about 100 years, finds ever-expanding applications in different fields of chemistry and in other experimental sciences. The present-day achievements of the method make it possible to investigate, e.g., processes with microgram quantities of a sample at temperatures of the order of 200°C, the kinetics and thermal effects of chemical reactions, etc. [1,2]. Of great interest is the use of DTA in investigations performed at high pressures. For a long time, however, DTA has been successfully used only to study melting and phase transitions at high pressures [1,3–8].

At the same time, the chemistry of high pressures has at its disposal a modest stock of experimental methods, owing to which most of the results in this field of chemistry have been obtained by the hardening and sampling methods. As to the attempts at investigating chemical reactions under pressure "in situ", these have been quite scarce: one can note such works as the piston displacement method [9], X-ray phase analysis [10], shear stress [11], where the use of complicated technological equipment is required.

In this connection, it appears to us that differential thermal analysis, as a relatively simple and universal method, can occupy one of the first places of techniques allowing investigation of chemical transformations "in situ". Indeed, DTA does not need detectors to be placed in the reaction volume, and imposes minimum requirements on the high-pressure unit design.

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For successful investigation of chemical reactions (specifically in systems with a heightened chemical activity) under high pressures it is necessary to solve a number of technical problems:

(1) assuring reliable sample insulation from the pressure-transmitting medium in an ampoule made of a material sufficiently inert with respect to the reagents;

(2) attaining a sufficient volume of the sample-containing ampoule for reliable control of the chemical and phase composition of the mixture before and after the reaction;

(3) raising the sensitivity of the method, primarily by reducing the temperature gradient between the standard and the sample.

In previous work [12–16], we applied DTA techniques, in contrast to those previously described, to investigate, under high-pressure conditions, the chemical reactions taking place with such active substances as molten alkali metals and xenon difluoride. A detailed description of these techniques and the principles of their application are given for the first time in the present communication.

DTA AT HIGH QUASI-HYDROSTATIC PRESSURES

The technique used in refs. 12–14 has made it possible to study the reaction of lithium, sodium and potassium implantation in graphite in the 2–8 GPa pressure range at temperatures up to 350 °C. This was performed in a quasi-static-pressure apparatus of the "toroid" type [17]; the DTA cell assembly is shown in Fig. 1.

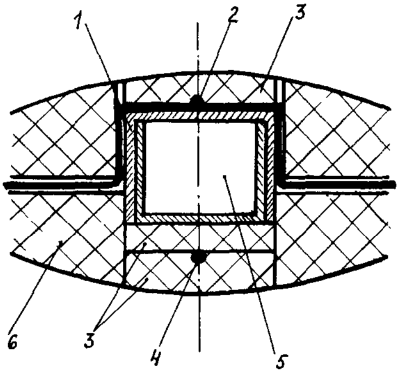

Fig. 1. DTA cell assembly in a high quasi-hydrostatic pressure chamber: 1, self-packing ampoule; 2, sample thermocouple; 3, heat-insulating discs (pyrophyllite); 4, standard thermocouple (perpendicular to the figure plane); 5, sample; 6, "toroid" container.

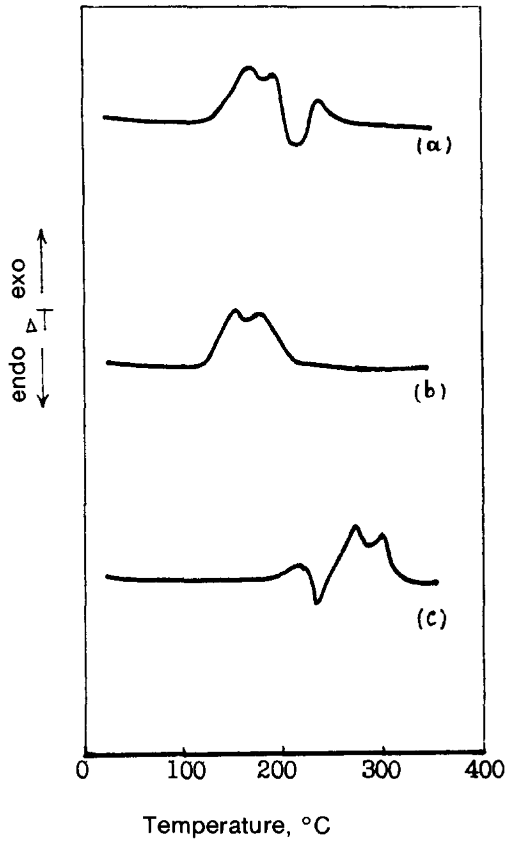

Fig. 2. DTA curves on heating in the graphite–lithium system: (a) C/Li = 6, $P = 3$ GPa; (b) C/Li = 6, $P = 6$ GPa; (c) C/Li = 2, $P = 4$ GPa (sample not a mixture of powders but discs of graphite and lithium).

Hermetic sealing of the ampoule with the sample was achieved with a simple self-packing device proposed in refs. 3 and 18 consisting of metal cups inserted into one another.

A heightened sensitivity of the method and an increase in sample volume was successfully achieved by using external, not internal as in refs. 3 and 4, heating of the high-pressure apparatus. In particular, this allowed an increase in reaction volume by ~ 10 times, improving cell reliability and isothermicity, etc.

When studying the interaction of alkali metals with graphite the investigated mixture was heated at a certain pressure, with the chemical reaction observed on the DTA curve, superimposed on the metal melting effect. The corresponding curves for the graphite–lithium system are shown in Fig. 2. Mixtures of different compositions were studied at the same pressure. If the alkali metal was taken in excess with respect to the stoichiometry of the implantation compound C_xM, the effect of metal crystallization from the

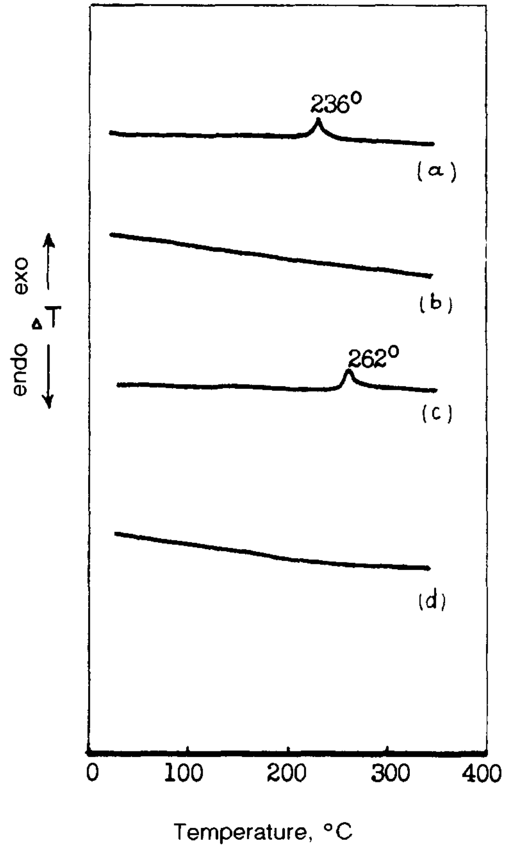

Fig. 3. DTA curves at cooling after the termination of chemical reaction between graphite and lithium or potassium, $P = 4$ GPa: (a) C/Li = 1.8; (b) C/Li = 2.1; (c) C/K = 3.8; (d) C/K = 4.2.

melt (see Fig. 3) was observed on the cooling curve after termination of the chemical reaction. By conducting a series of experiments at each pressure value in question, the $x(P)$ dependence, described in refs. 12–14, was obtained.

Since the task is to record the effect exerted by the melting or crystallization of residual reagent quantities, the high sensitivity of the technique becomes particularly significant, which we increase even further by using hydrostatic pressure in the apparatus.

DTA AT HIGH HYDROSTATIC PRESSURES

For investigations in the pressure range up to 1.2 GPa we have developed a quantitative DTA technique in a hydrostatic-pressure unit with a silicone fluid serving as the pressure-transmitting medium. With the help of this

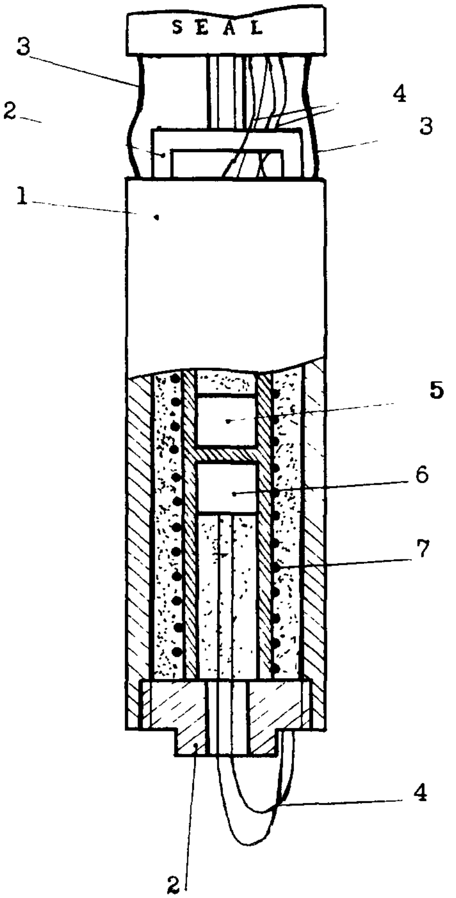

Fig. 4. DTA cell in a high hydrostatic pressure unit: 1, cell body; 2, plugs; 3, power outlets of the furnace; 4, thermocouples; 5, holder of the standard; 6, holder of the sample; 7, furnace.

technique the interaction in the graphite–lithium and graphite–potassium systems at pressures up to 0.8 GPa and temperatures up to 350°C was studied [15]. The DTA cell is shown in Fig. 4.

In hydrostatic units, in contrast to solid-phase apparatus, it is impossible to use self-packing ampoules for the samples. Consequently, the problem of ensuring sample insulation from the pressure-transmitting medium is particularly important. We have tested different design modifications, and the optimum one is shown in Fig. 5. A feather-edge seal with a metal gasket has been used, providing hermetic sealing up to temperatures of about 400°C and pressures of 1.2 GPa. Good reproducibility between one experiment and another of the conditions of heat transfer from the sample to the thermocouple (standard deviation of the calibration coefficient not higher than 6%) allowed the use of this technique in quantitative DTA. The chosen design, in

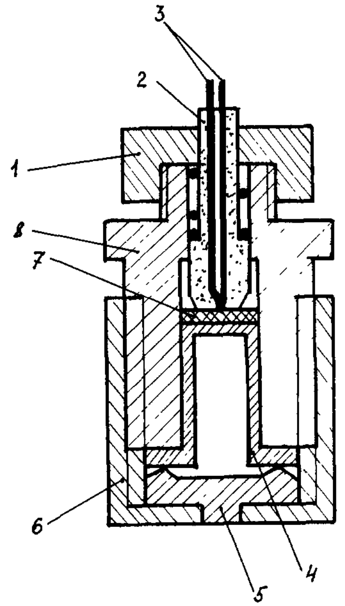

Fig. 5. Sample holder: 1, nut (brass); 2, conductor for the thermocouple with a spring (pyrophyllite); 3, thermocouple; 4, cup with sealing rim (copper); 5, ring-shaped knife (steel); 6, holder cartridge (steel); 7, washer (mica); 8, clamping screw (steel).

contrast to those described previously [5–8], allows the investigation of relatively large samples (up to 0.5 g).

It is now possible to measure the quantity of reagent spent or product accumulated, in the high-pressure cell, which could not be done in the "toroid" apparatus. Figure 6 shows the curve of lithium consumption on reaction with graphite, obtained with the present technique. To control the

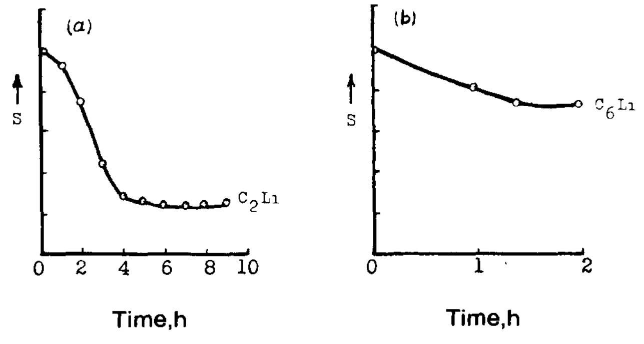

Fig. 6. Variation of lithium melting effect area on the DTA curve in the course of synthesis: (a) C/Li = 1.5, $P = 0.8$ GPa, the compound formed is C_2Li; (b) C/Li = 1.5, $P = 0.2$ GPa, the compound formed is C_6Li.

course of reaction the cell was cooled at regular intervals below the melting point of lithium, and the crystallization effect was observed. Based on the area of the effect the mass of the melting material was calculated.

The possibility of using quantitative DTA to measure the mass of the melting material in the high-pressure cell is substantiated as follows.

The value of the thermal effect Q is known [19] to be equal to

$$Q = \int_0^\tau A_Q \Delta\epsilon \, \mathrm{d}\tau = A_Q S \qquad (1)$$

where $\Delta\epsilon$ is the differential signal of thermocouples, proportional to the temperature difference between the standard and the sample, resulting from the heat output in the sample; A_Q is the calibration coefficient, individual for every cell, and in non-quantitative DTA techniques, for every experiment; S is the area of effect on the DTA curve.

A_Q depends on temperature, and in the high-pressure unit on pressure as well.

In the case of a monovariant phase transformation (e.g., melting) the enthalpy variation ΔH is uniquely assigned by only one of the two thermodynamic parameters: temperature and pressure, i.e., from eqn. (1) can be obtained:

$$m = \frac{A_Q S}{\Delta H} = A_m S \qquad (2)$$

where m is the mass of the matter taking part in the transformation; A_m is

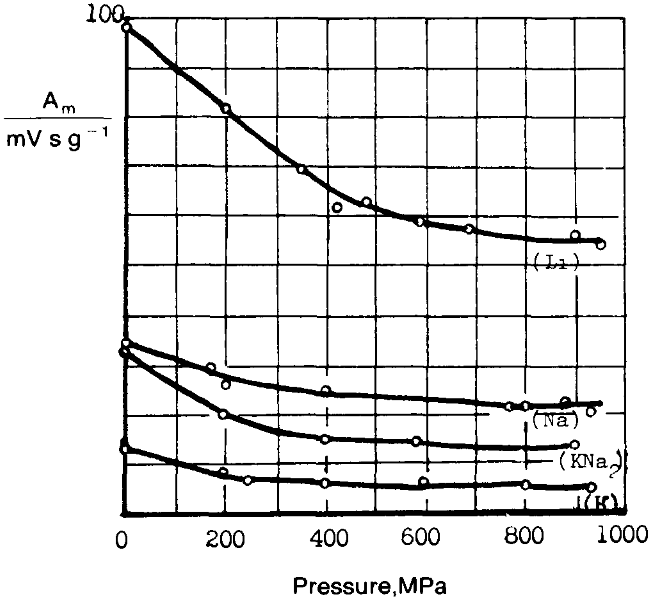

Fig. 7. Pressure dependence of the mass calibration coefficient A_m from formula (2) for the melting of alkali metals and the incongruent melting of KNa_2 intermetallide.

the mass calibration coefficient, individual for every substance and depending on pressure. From eqns. (1) and (2) it is seen that the unknown m can be determined from the area of the effect S and the data of calibration by the A_m pressure dependence.

In the present work the A_m coefficients were determined at different pressures for the melting of lithium, sodium and potassium, as well as for incongruent melting of the KNa_2 metallide. The calibration curves are shown in Fig. 7.

DISCUSSION

This work shows the strong possibilities opened up by the DTA method in chemical investigations under pressure. The techniques developed make it possible to solve experimental problems, not only on the systems with alkali metals studied here. Owing to the fact that the detector (thermocouple junction) in DTA can be placed outside the sealed ampoule containing the investigated mixture, it is possible to work with different types of aggressive systems. In particular, using aluminium as the cup material in the hydrostatic DTA unit, we studied the melting of a "superoxidizer", xenon difluoride. Data have been obtained on the melting curve of XeF_2 up to 0.8 GPa * (m.p. = 278°C). In addition to observing the melting effect, it is also possible to study chemical reactions in which one of the reagents is a solid undergoing a phase transition under pressure.

There are additional possibilities for the range of pressures and temperatures in DTA using hydrostatic pressure. Substitution of argon for silicone fluid will allow an increase in maximum temperature up to at least 1000°C. The use of techniques in which the pressure-transmitting gas simultaneously constitutes a reagent, as described in ref. 20, also appears promising.

The use of DTA under pressure should produce the greatest effect when combined with other experimental methods. For instance, the combination of quantitative DTA with the current method of calorimetry under pressure (see ref. 21).

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