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Abstract

Full Text

PHYSICAL CHEMISTRY

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DIFFERENTIAL-THERMAL ANALYSIS AT PRESSURES UP TO 100 kbar*

As is known, first-order phase transitions are accompanied by a step-like change in volume and by thermal effects, which are determined by the Clausius–Clapeyron equation:

$$dT/dp = T\Delta V/\Delta H.$$

In investigations at high pressures, polymorphic transitions are most often recorded by the piston-displacement method (from the volume jump ΔV) or from the jump in electrical resistance. The method of differential-thermal analysis (d.t.a.), which makes it possible to record first-order phase transitions by their thermal effect and also to determine quantitatively the magnitude of the thermal effect, has begun to be used for studying $P–T$ diagrams of various substances at high pressures only in the last decade, but already at the present time has found fairly wide application in the work of many researchers both in our country and abroad.

Under hydrostatic-pressure conditions up to 34 kg/cm^2 and at temperatures up to 800° by the d.t.a. method, the heats of polymorphic transitions in metallic cerium and bismuth were determined and their phase diagrams studied; melting curves of several metals were also investigated ([1–4]). E. G. Ponyatovskii and coworkers carried out a study of the phase $P–T$ diagrams of the Fe–C system at pressures up to 30 kbar and temperatures up to 1000° K ([5]), and also of the Bi–Sn system at lower temperatures ([6]).

Fig. 1. Schematic of the introduction of a differential thermocouple into a high-pressure chamber.

Fig. 2. Summary thermogram for various substances

Figure 2: Fig. 2. Summary thermogram for various substances

1 –talc cover;
2 –metallic bismuth;
3 –talc insulating screen;
4 –Teflon or talc washer;
5 –differential chromel-alumel thermocouple;
6 –substance under study;
7 –pressure-transmitting medium

Recently Kennedy and coworkers have carried out a number of studies on the investigation of phase diagrams of both metals and binary compounds of elements of groups II–VI and III–V up to pressures of 70 kbar and temperatures up to 1200°. The method of investigation is described in ([7]), in which the authors point to the impossibility of accurately recording, by the d.t.a. method, polymorphic transitions of the type solid phase I–solid phase II because of the insufficient sensitivity of the method; therefore these regions of the phase diagrams were studied by the piston-displacement method.

In connection with the foregoing, we developed a method for recording first-order polymorphic transformations in the solid phase by the d.t.a. method up to pressures of 100 kbar at room temperature. The construction with which the investigations were carried out is shown in Fig. 1.

The readings of the differential chromel-alumel thermocouple were recorded by a low-frequency thermographic recorder (NTR-63) with

* On the basis of the materials of this article, a report was presented at the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry on February 10, 1965.

by photographic recording. The charges of the substances under investigation were 0.05–0.1 g.

Figure 2 shows thermograms of bismuth, cerium, barium, and silver chloride.

For determining the sign of the thermal effects of the polymorphic transitions of the substances under investigation, metallic bismuth was placed near the second junction of the differential thermocouple as the reference substance. It was shown that the transition in metallic bismuth (89 kbar) is endothermic, whereas those in metallic barium (59 kbar), in silver chloride (88 kbar), and in metallic cerium (7 kbar) are exothermic.

Fig. 2. Summary thermogram for various substances

The polymorphic transition for barium (17 kbar), noted by Bridgman ([8]), and cerium (50–70 kbar), assumed by L. D. Lifshits, Yu. S. Genshaft, and V. I. Markov ([9]), was not detected.

This method can be used successfully not only as a method for calibrating a chamber with respect to pressure, instead of the electrical-resistance method, but also for estimating the very magnitude of the thermal effect with more or less satisfactory accuracy. It is intended in the future to carry out quantitative estimates of the magnitudes of the thermal effects of certain polymorphic transitions at high pressures.

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Note: Figure translations are in progress. See original paper for figures.