THERMOCHEMISTRY AND STRUCTURE OF ATOMS

COMMUNICATION 7. INVESTIGATION OF THE CARBONATES OF THE
SECOND (MAIN) GROUP OF THE MENDELEEV SYSTEM

A. F. Kapustinsky and M. S. Stakhanova

INTRODUCTION

Consideration was given in one of the preceding communications to the application of the rule of thermochemical logarithmicity[1] to oxalates of alkaline earth metals[2]. In the present paper we develop the investigation with reference to the carbonates of the same elements in view of the particular practical and theoretical importance of these compounds in metallurgy, in the chemistry of building materials and in geochemistry. This paper includes in part the results not only of calorimetric measurements but also of our earlier determinations (made with the help of other methods) of thermodynamic constants of the carbonates of beryllium[3] and strontium[4,5]. The critically carried out systematization of the experimental data enabled the thermodynamics of the above-mentioned carbonates to be summarized; it also permitted the constants obtained to be generalized in the light of the rule of thermochemical logarithmicity and allowed a number of conclusions about the properties of the carbonate ion to be drawn.

The thermodynamics of the alkaline earth carbonates has been dealt with by many investigators, but in the majority of cases the measurements are not sufficiently accurate so that not only do serious discrepancies arise in the same type of measurements but there are unexplained deviations between calorimetric and high-temperature determinations of thermodynamic constants. This is illustrated by the monograph (documented in detail) of Kelley and Anderson[6]. Since the publication of the latter work, no substantial changes have taken place in this field, which circumstance made it not only desirable but even necessary that the present investigation should be undertaken.

EXPERIMENTAL

1. METHOD OF INVESTIGATION

Heats of formation were determined by studying the thermal effects of dissolution of finely crystalline (synthetic) MgCO₃ and BaCO₃ in 1 M solution of HCl at 25°C. The hydrochloric acid was previously saturated with carbon dioxide at atmospheric pressure. The correction for evaporation of water was made as in the paper of Kapustinsky and Desideryeva[4]. In the case of MgCO₃ special attention was given to determination of the heat of solution of MgO in HCl.

The following changes were made in the calorimeter previously described by Kapustinsky and Klokhman[7]. The thermostat was a Bose casing supplied with water from an adjacent thermostat with the aid of a water turbine. The temperature of the thermostat was maintained at 25 ± 0.005°C. Current (120 V) was applied (Fig.1) to the heating spiral of the thermostat H; a vacuum relay VR was connected in series. The winding of the latter was connected to the tube (6F6) of an electrical relay whose heating circuit was supplied by the step-down transformer T, while the anode circuit was fed from the 120 V mains. Under normal emission the vacuum relay was switched in. On closing the contact of the thermoregulator TR (25°), however, the tube circuit was short-circuited, the amplification of the emission led to amplification of the current in the series winding of the vacuum relay, which broke the contact in the main circuit and cuts out the heating spiral. The fall of temperature leads to closing of the circuit opening through the thermoregulator and consequently to resumption of heating. Since the current strength in the anode-mains circuit does not exceed 5-10° A, there is no risk of burning-out of the contacts and of damage to the thermostat.

The calorimeter was a pyrex glass beaker, volume 0.45 l, closed with an ebonite stopper through which passed a Beckmann thermometer, a glass propeller stirrer, the leads of a Vrevesky mercury spiral, a glass tube with a bulb at the end containing a weighed amount of the substance, and a thin test tube for introduction (if needed) of freezing.
mixture. The energy introduced for determination of the heat capacity of the solution was measured with the help of a potentiometric circuit which enabled alternate measurement of the voltage at the terminals of the divider and of standard resistance at definite intervals throughout the main period. The electrical measuring circuit (Fig. 2) consisted of a Rapp potentiometer $R_{1}$, a standard Weston element $R_{2}$, a 1-ohm standard resistance $R_{stand}$, a resistance box $R_{1}$, $R_{2}$, and a mirror galvanometer $G$ with a sensitivity of $10^{-6}$ A. In the diagram are also shown the calorimeter heater $R_{spir}$, the loading resistances $R_{load}$, the rheostats $R_{1}$, $R_{2}$, the ammeter $A$, the switch and circuit switches $k_{1}$, $k_{2}$ and a battery of lead accumulators (6V). Current strength and voltage were measured to an accuracy of 0.0001 A and 0.0001 V for total effects of the order of 0.8 A and 0.5 V.

The temperature was measured with a Beckmann thermometer (calibrated against a standard instrument in VIMS) with the aid of a cathetometer to an accuracy of $0.001^\circ$ for a rise of the order of 0.4$^\circ$; the time was measured to an accuracy of 0.1 seconds for periods of 3 to 4 minutes. All the electrical measuring instruments were checked before the start of the work in the Weights and Measures Department and were provided with certificates. The stopwatch was regulated against an accurate time signal; it was connected to the circuit by the usual switch scheme [8]. The operation of the apparatus and the introduction of corrections for radiation, also the mode of computation, are as described in the literature [7, 8, 9].

The apparatus was calibrated by an electrical method and against the heat of solution of potassium chloride. At the conclusion of an experiment, the temperature of the calorimeter was brought to the initial temperature and the water equivalent of the system was determined in conditions similar to those prevailing for determination of heats of solution. The accuracy of the determinations (heats of solution), allowing for the characteristics of the instrument that we used, the amounts of heat evolved and the weights of reagents, ranged from 0.6 to 1.6% (with MgO and MgCO$_3$) and to 3% (with BaCO$_3$).

A special place is occupied by the thermal investigation of beryllium carbonate which we described elsewhere [3] and the results of which are set forth in this paper. As is usual in investigations of dissociation equilibria, accurate allowance for all factors is impossible and moreover calorimetric measurements are impracticable, in this case. Nevertheless we consider it to be necessary to again draw attention to the arguments in support of the trustworthiness of our previous investigation: a) satisfactory maintenance of the linear dependence of log $K$ on $1/T$; b) reproducibility of the results on approach to equilibrium both from the low- and the high-temperature side; c) non-dependence of the results on the degree of reduction of the weighed specimens (indicating absence of solid solutions); d) the crystallinity of the substances, confirmed both by microscopic and by X-ray examination (Fig. 3). The same may be said about the investigation of SrCO$_3$. An approximate evaluation in both cases gives an accuracy of determination of the heats of dissociation of 5 - 7%.

2. STARTING SUBSTANCES

a) Beryllium carbonate. We have already published a short account of the investigation of beryllium carbonate [3]. Here we limit ourselves to giving the X-ray diagram (Fig. 3) which testifies to the crystallinity of the material used.