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Review

Test and calibration processes for the differential reaction calorimeter (DRC): Application: Dissolution of calcium fluorapatite in the hydrochloric acid

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ABSTRACT

Changes were performed on the apparatus of the differential reaction calorimeter (DRC) in order to get higher sensitivity. The performance of this simple instrument was tested by measuring the enthalpy of dissolution of the trihydroxymethyl aminomethane, $(HOCH_2)_3CNH_2$, or "THAM" in 240 g of 0.1 mol L^{-1} hydrochloric acid at 298 K. We used the joule effect to calibrate the DRC and a statistical treatment to adjust the coefficients of calibration curves.

DRC was also used to achieve the dissolution of the synthesized calcium fluorapatite, $Ca_{10}(PO_4)_6F_2$, in hydrochloric acid for different concentrations at 298 K. Two solution mechanisms were suggested for different pH ranges and therefore the enthalpy of dissolution of $Ca_{10}(PO_4)_6F_2$ in pure water was deduced.

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1. Introduction

A new differential reaction calorimeter (DRC) has been launched by SETARAM and developed by Aventis Pharma in their own laboratories to optimize the industrial processes and the safety of chemical reactions. This apparatus is based on the work of Baumgartner and Duhaut [1] and Küssner [2] and gives fast access to thermodynamic data, such as reaction heat, heat flow and heat capacity. Since the experiments required large quantities of product (not less than 10 g), we were obliged to modify this equipment so as to increase the sensitivity of DRC and therefore to reduce waste from the used product by making it sensitive to a few milligram ones. The performance of DRC was tested by dissolution reaction of THAM in the hydrochloric acid whereas the calorimeter calibration was carried out by electrical effects.

Actually, the statistical treatment of the obtained values by calorimeter was so important, which not only helped us to determine the coefficients of calibration curve used for measured values but also to be sure that the experimental errors had no significant influence on these measurements. The calibration of calorimeters has, indeed, been the focus of many studies [3,4] interested in the development of the statistical treatment which determines the calibration coefficient [5] useful for values experimentation.

The importance of apatite in various fields, particularly fluorapatites, drew our attention to understand their fundamental chemical properties. Their behavior in water is of major importance even though they are poorly soluble in such solvent. The solution mechanisms of synthetic phosphates in aqueous milieu were not deeply studied. Some researches on the dissolution of hydroxyapatite in acid solutions were conducted [6], whereas the dissolution of fluorapatite in acid solutions studies focus mainly on the area of kinetics [7,8]. Besides, the calorimetric technique was suitable for the study of phosphates thermodynamic properties [9] whereas the dissolution enthalpy in pure water could not be directly obtained.

As a matter of fact, this work aims to describe and calibrate the calorimeter, develop the statistical method used for the experimental results and to determine the solution mechanisms of fluorapatite, $Ca_{10}(PO_4)_6F_2$, or CaFap in hydrochloric acid solution with various concentrations, and finally to deduce the value of enthalpy of dissolution of CaFap in water.

2. Experimental

2.1. Instrument design and function

The DRC works according to the isoperibolic mode and is essentially based on the continuous measurement of the temperature difference between two glass reactors, thermostatted at the same constant temperature during the experiment. A fluid circulates in the double jacket of the reactors and the fluid temperature is controlled using a thermostatic bath (temperature stability at ±0.1 °C). The sample is deposited in a cylindrical tube made of hard plastic (14 mm of diameter and 120 mm of length) closed on two sides by parafilm (sample holder). The samples holder should be immersed in the solvent that is in the reactors. The calorimeter also comprises a central rotating agitator in both reactors. The used stirring rate is of (200 turns/min) and is fixed with a motor (Fig. 1).

At first, this calorimeter was not sensitive to low thermal effects (almost 20 J) and few changes took place in our laboratory. Hence, to achieve a higher sensitivity, we decided to change the Pt-100 thermometer with the use of two thermocouples "Chromel-Allumel" which were themselves connected to an amplifier type Microvoltmeter 150B of sensitivity from 1 mV attached to a multi-meter type Keithley 2182A with a digital output transforming the temperature variations into proportional ones with a potential difference or "ddp" (see Fig. 1).

The outbreak of the reaction took place after a long time, about three hours, during which a thermal equilibrium was established between the thermostatted fluid flowing in the double jacket of the reactors and the solvent which was inside them. Accordingly, the two reactors nearly had the same temperature. At the beginning of the experiment, both of the reaction and reference vessels contained the same amount of solvent, the same stirring anchor and rate with the same internal accessories to ensure a very close transfer coefficients. Then the product was introduced to the reaction vessel by drilling the parafilm of the sample holder through a glass needle and no sooner did the chemical reaction start, than the difference in temperature was recorded between the reaction vessel and the reference one.

Yet, in the reference vessel, there was no reaction. The Joule effect calibration was applied through a platinum resistance calibration probe. The curve of the ddp between the two reactors was recorded versus time.

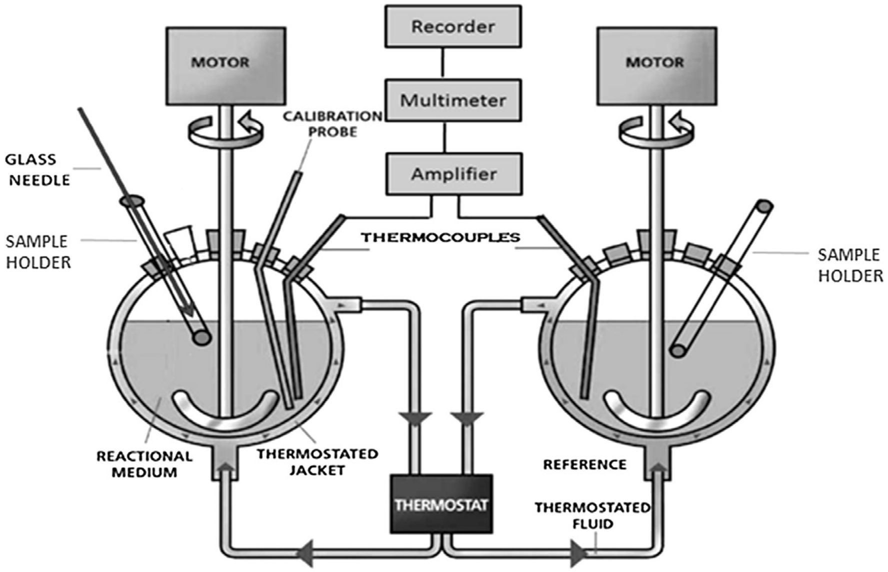

Fig. 1. The DRC after modification.