

## Applications

### Real-Time Measurement System for High-Temperature Drop Calorimeter

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**Abstract:** *The paper deals with the description of the design and function of a high-temperature drop calorimeter for measuring of increases in enthalpy of solids and liquids between a chosen temperature in the range of 1200-2000 K, and 298 K. The samples have a volume of 1.0-1.2 cm<sup>3</sup> and are placed in PtRh10 crucibles with 10 mm in diameter and 13 mm in height. The sample temperature in the furnace is measured by a PtRh6-PtRh30 thermocouple. The calorimetric block proper has a capacity of  $3.8876 \pm 3.6 \times 10^{-3}$  kJ.K<sup>-1</sup>. The heat energy increase values in the range of 1800-3000 J are measured with an error of 5 J.*

*Our task was to design a modern method of measurement and processing data from the drop calorimeter and its management options based on Windows operating system working in real time.*

**Keywords:** *RXT OS, drop calorimeter, unbalanced Wheatstone bridge.*

#### 1. Introduction

Since the temperatures, under which the materials are produced and used continue to rise, the need for an improved high-temperature thermodynamic database increases as well. The improvements in the measuring equipment have been a part of the response to this need; so that the development of improved high-temperature calorimeters has been particularly important. A good high-temperature calorimeter must:

- operate at as high temperature as possible;
- make measurements quickly, accurately, and reproducibly;

- minimize the interactions between the material being tested and the environment, in which the testing occurs;
- be usable for a variety of thermodynamic measurements, including measurements of heat capacity, enthalpies of transition (phase changes, melting), and enthalpies of reaction.

Several types of high-temperature calorimeter have been used for these purposes. The calorimetry methods used are drop, adiabatic, pulse, differential scanning, and the newest method, high-temperature differential scanning [1-7].

Drop calorimetry is the method, by which most of the high-temperature heat capacity data in literature have been determined. In drop calorimetry, a small sample heated to a known temperature outside the calorimeter is rapidly dropped into the cavity of a well-insulated (and much larger) calorimeter block, also at a known initial temperature. The increase in the temperature of the calorimeter block when it reaches equilibrium with the sample, determines the sensible heat of the sample, relative to the final temperature. Repeated drops from different sample temperatures determine a curve of sensible heat vs. sample temperature; the derivative of this curve with respect to the temperature calculates sample heat capacity at a given temperature [8-10].

Drop calorimetry has few temperature limitations and can use any type of a sample container. For refractory metals, levitation calorimetry can be used to eliminate the sample holder altogether. On the other hand, it is extremely slow, makes only one measurement of sensible heat at a time, and does not have the best reproducibility. The need to determine heat capacities as the derivative of a sensible-heat curve reduces the accuracy. Enthalpies of transition can be measured if the sample goes through the required phase change on quenching in the calorimeter block; if quenching occurs too quickly, this may not happen.

The drop calorimeter described in the present paper is designed for the measurement of increases in enthalpy of solid or liquid samples 1.0-1.2 cm<sup>3</sup> in a volume between temperatures in the range of 1200-2000 K and 298 K. It allows measurement under reduced or atmospheric pressure; when choosing the working pressure value it is necessary to take into account the dependence of the specific heat conductivity of the gas considered on pressure.

## 2. Description of the apparatus

The calorimetric apparatus (Fig. 1) consists of the following three basic parts: the furnace I, the connecting tube II, the calorimetric block III.

The situating of the crucible with the sample, and that of the sample temperature measuring thermocouple, is shown in Fig. 2. The crucible suspension is passed through the holes of the degussite capillary tube A, which is held in a recess at the end of tube IV (Fig. 1) by PtRh10, diameter 0.3 mm wire. This wire passes through one of the capillaries of tube A and its end is inserted into the capillary of tube IV. The thermocouple joint sensing the crucible temperature is inserted into the recess of the two-capillary ceramic tube B. The distance of the joint from the crucible lid is about 2 mm. The crucible is 10 mm in diameter and 13 mm in height.

It is heated in the zone of homogeneous temperature (approximately at the furnace center) which has width of about 2 cm. The difference between its maximum and minimum temperature is about 1 K. A PtRh18 (PtRh6-PtRh30) thermocouple was used for measuring the sample crucible temperature in the furnace.

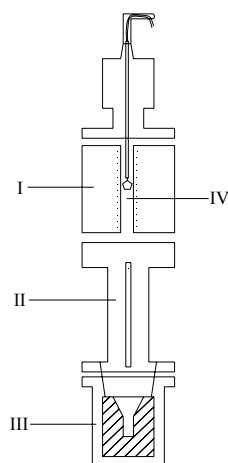


Fig. 1. Schematic diagram of the drop calorimeter

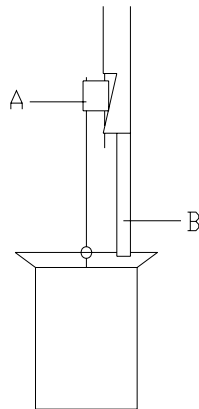


Fig. 2. A detail of the sample crucible suspension

The design of the calorimetric block was based on the study presented in [11].

The copper calorimetric block (mass about 10 kg, Fig. 3) consists of two parts mutually pressed-in together. The calibrating manganine winding 4 is placed at the surface of the interior part 3 in milled grooves. In similar grooves on the surface of the external part 2 there is found the winding of the thermomentering resistance bridge 5 embedded in epoxy resin. The epoxy coating improves the heat transfer from the block into the winding and protects the latter from mechanical damages. Approximately at the block center, screen 15 passes through a slit in the block; the

screen is shifted by a spring, which in turn is fixed by screw 14. The screen is adjusted to its starting position through handling opening 6 and is released by attraction of core 11 of electromagnet 13 with a counterspring 12. The supply wires for the two windings and the block electromagnet are passed to connector 7.

The block is suspended at three points of the bottom part of the connecting tube from suspension 9 passing through the eyes of screws 8. Jacket 1 is immersed up to its flange in water in the ultrathermostat, in which the temperature is maintained at  $298 \pm 0.003$  K.

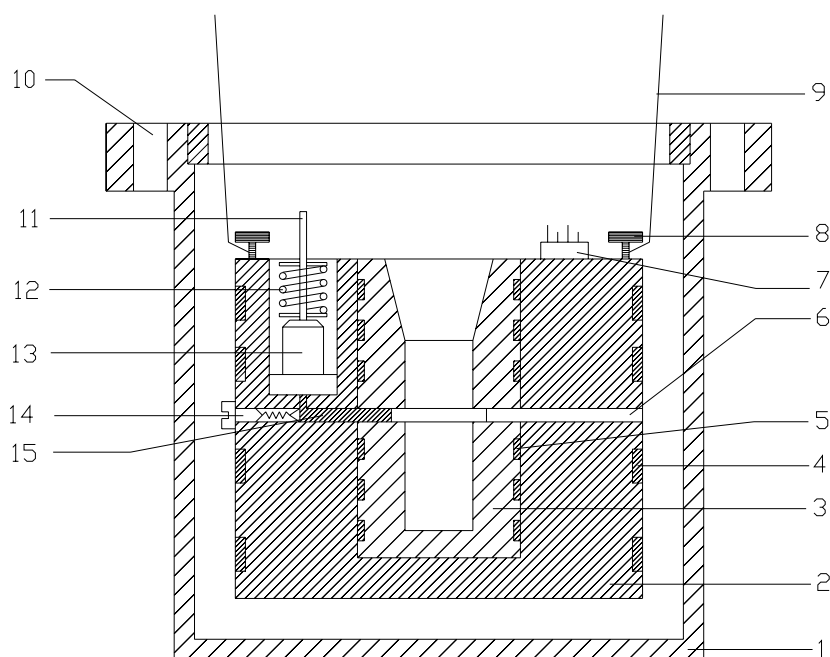


Fig. 3. Schematic diagram of the calorimetric block

### 3. Temperature measurement

The increase in the calorimetric block temperature due to cooling down by the crucible that has been dropped from the furnace, amounts to about 0.6 K.

The calorimetric block temperature was measured with an unbalanced Wheatstone bridge, the opposite resistors of which were made of temperature-dependent material (copper wire, dia. 0.1 mm), the other couple of the opposite resistors being practically temperature-independent (manganine wire dia. 0.1 mm). The bridge is almost symmetrical; its resistances measured at 296 K have the respective values  $R_{10} = 1364 \Omega$ ,  $R_2 = 1377.2 \Omega$ ,  $R_2 = 1377 \Omega$  and  $R_{40} = 1364.3 \Omega$ .

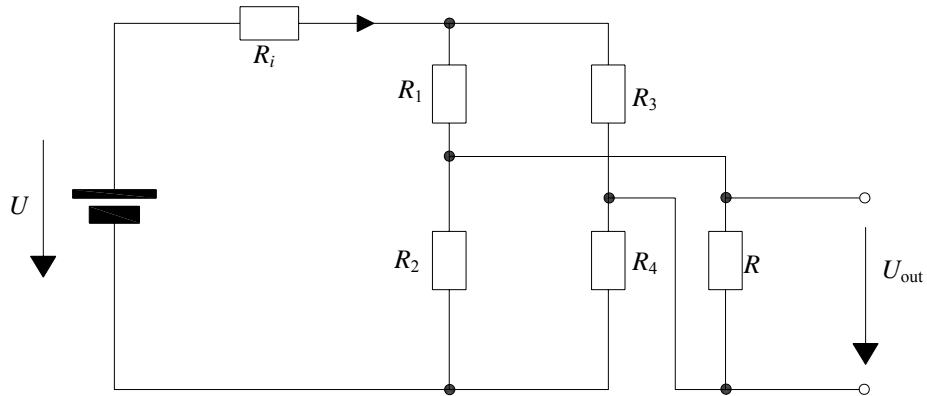


Fig. 4. Schematic diagram of the Wheatstone bridge measuring the temperature of the calorimetric block

General analysis of the unbalanced Wheatstone bridge (Fig. 4) yields, under the condition that the bridge is supplied by constant current  $I$  (so that  $R_i \rightarrow \infty$ ) and the bridge measuring diagonal is unloaded ( $R \rightarrow \infty$ ), the following relationship for the output bridge voltage

$$(1) \quad U_{\text{out}} = -I \frac{R_1 R_4 - R_2 R_3}{R_1 + R_2 + R_3 + R_4},$$

$$(2a) \quad R_{1(T)} = x_{(T)} R_{10},$$

$$(2b) \quad R_{4(T)} = x_{(T)} R_{40},$$

where  $R_{10}$  and  $R_{40}$  are the values of these resistors at any arbitrarily chosen relative temperature and  $X_{(T)}$  is a function of temperature, which indicates their temperature dependence.

After substituting (2a), (2b) in (1) and rearrangement it follows:

$$(3) \quad U_{\text{out}} = -I \frac{R_{10} R_{40}}{R_{10} + R_{40}} \frac{x_{(T)}^2 - \frac{R_2 R_3}{R_{10} R_{40}}}{x_{(T)} + \frac{R_2 + R_3}{R_{10} + R_{40}}}.$$

When taking

$$(4) \quad \sqrt{\frac{R_2 R_3}{R_{10} R_{40}}} = \frac{R_2 + R_3}{R_{10} + R_{40}}$$

and rearranging, one obtains the condition

$$(5) \quad (R_{10} R_2 - R_3 R_{40})(R_2 R_{40} - R_{10} R_3) = 0.$$

To make relationship (5) hold, e.g., the following condition should be complied with

$$(6) \quad \frac{R_{10}}{R_{40}} = \frac{R_3}{R_2} = k,$$

where  $k$  is the relative value of the resistances. Then the relation (3), using (6) and after rearrangement acquires the form

$$(7) \quad U_{\text{out}} = -I \frac{1}{1+k} [R_{1(T)} - kR_2].$$

Within the temperature range of 273-373 K the resistance of the copper conductor can be considered perfectly linear in terms of temperature, so that even the relationship  $U_{\text{out}} = f(T)$ , given by relation (7) is linear in the working temperature region.

A block diagram of the instrument, measuring the calorimeter temperature, is shown in Fig. 5.

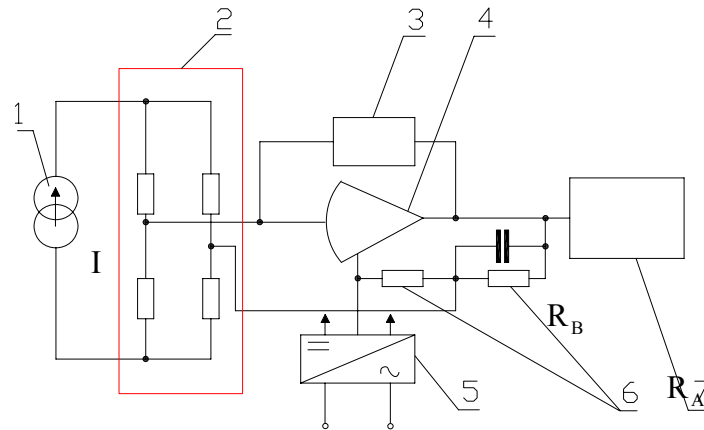


Fig. 5. Block diagram of the thermometry apparatus for measuring the temperature of the calorimetric block

The source of constant current  $I = 232 \mu\text{A}$  (1) feeds one diagonal of the thermometry bridge (2). The bridge output voltage is amplified by a unidirectional microvoltmeter, which consists of a voltage limiter (3), a type AS101 operational amplifier (4) and operational impedances (6). Such a series connection of the operational amplifier has an input resistance of the order of  $10^{11} \Omega$ , so that the condition of currentless measuring is well complied with. The microvoltmeter amplification is preset by operational impedances at  $A = -1000$ .

The output of the amplifier is measured by type S2700 digital multimeter (Keithley) (7).

The temperature sensitivity of the measuring apparatus is  $600 \text{ mV.K}^{-1}$ .

At 298 K electric input introduced into the thermometry system is  $N = 1.6 \times 10^{-7} \text{ J.s}^{-1}$ , to which, considering the mean thermal losses from the block into environment, corresponds a stable temperature gradient of  $3.5 \times 10^{-4} \text{ K}$ . This value can be neglected because the resolution sensitivity of the thermometry

apparatus is  $\pm 5 \times 10^{-4}$  K. The supplementary electric input into the calorimetric block, resulting from the increase in bridge resistance at a change of its temperature by 1 K causes a temperature determination error of about  $8 \times 10^{-7}$  K. This error needs not likewise be taken into account.

#### 4. RT System

RTX is specifically designed as a real-time extension to the Windows operating system. It is not an RTOS ported to Windows. RTX provides precise control of IRQs, I/O, and memory to ensure that specified tasks are executed with proper priority and 100 % reliability. By operating in Ring 0, RTX ensures the highest performance and requires minimal configuration, supporting sustained interrupt rates of 30 kHz with an average IST latency of less than one microsecond [12-14].

RTX architecture is a true extension in that it does not encapsulate Windows and does not interfere with, or modify any of Windows infrastructures. By maintaining this separation, the RTX real-time sub-system (RTSS) ensures that RTX-based applications survive Windows crashes or “blue screens”.

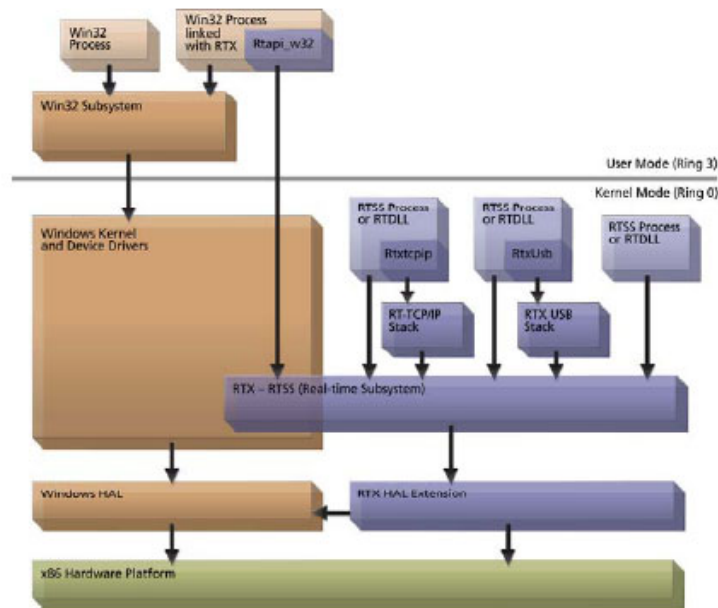


Fig. 6. Rtx subsystem architecture [15]

#### 5. Conclusion

In this paper we described how to use real-time operating system in a system of a high-temperature drop calorimeter for measuring the increases in enthalpy.

With the use of real-time priorities, we have shown that it is possible to improve the stability of certain real-time tasks.

The prototype system described in this paper provides a suitable tool to experiment with different user-level scheduling schemes. The heartbeat timer can be effectively used for such user-level scheduling.

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