

A New Versatile Semiconductor Calorimetric System for Solution Calorimetry

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Abstract

In this work the combination of the refrigeration technique by semiconductors with calorimetry is proved to be effective through the development of a versatile semiconductor calorimetric system and the calorimetric measurements with it. Self-made semiconductor thermoelectric sensors and a semiconductor thermostat were used in this calorimetric system. The thermostat operates in a temperature range from 0 to 60°C. The sensitivity of the sensor is 25 mV K⁻¹ (not amplified). The versatility of this system has been demonstrated in the ability to make precision measurements in adiabatic or in isoperibol mode. The precision of measurements is about 0.06%. The value for the specific heat capacity of water, c_p (298.15 K), was obtained to be $(4.176 \pm 0.013) \text{ JK}^{-1} \text{ g}^{-1}$ for measurements with the adiabatic calorimeter, and for the enthalpy of solution of KCl, $\Delta_{\text{sol}}H(200 \text{ H}_2\text{O}, 298.15 \text{ K})$ was $(17.56 \pm 0.01) \text{ kJ mol}^{-1}$ for measurements with the isoperibol calorimeter. These results are in good agreement with the values recommended by the Physical Chemistry Division of IUPAC in 1974.

I. FUNDAMENTALS

The semiconducting materials used for refrigerating devices have high thermoelectric power, higher thermal emf and low thermal conductivities. Thermoelectric piles made of these materials can be used in a temperature range approximately from -100⁽¹⁾ to 400°C,⁽²⁾ and the working surface of it will change conveniently from cooling to heating state and *vice versa* only by reversing the current direction. These distinctive features will be powerful potentialities that can be brought into full play in calorimetry.

1. Adaptable to temperature control of surroundings.

Taking advantage of the special capability of heating and cooling at the same set of junctions of a refrigerating semiconductor thermoelectric pile, it is not difficult to provide for various types

of calorimeters an environment of required delicate temperature control, when connecting it into an appropriate controlling circuit.

The Peltier effect arises at the interface of two kinds of electrode materials with fairly low thermal conductivities. The heat capacity of the copper pieces usually used for conducting current is also small so that a very low thermal inertia of the working surface of thermoelectric pile will be obtained. Thus when in a state of cooling, it will go immediately to heating while the current direction is reversed. This implies that the thermal shock to the surface is transient on changing the working state and can be neglected. This is very important in implementing precision temperature control and has been proved true in our own work.

To ensure the recurrence of this performance of the thermoelectric pile used in calorimetry, a cylindrical construction of it composed of curved pieces of thermoelectric elements was designed by us and also a complete technology for constructing it developed.

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Moreover, the temperature range from -100 to 400°C is very important in calorimetry. A great deal of heat data necessary for theoretical research and in industry lies within this range. From the present achievements in material science and the state-of-the-arts, it is absolutely possible to carry out or improve the calorimetric measurements in this temperature range just by the refrigeration technique using semiconductors.

2. Monitoring temperature difference.

Temperature difference monitoring is important and done frequently in calorimetry, such as that in adiabatic calorimetry, differential calorimetry (twin calorimeters), conduction calorimetry (micro-calorimeters) and isothermal calorimetry, where sensitive detections of temperature differences between system and surroundings are necessary. In view of the fact that the above mentioned materials have Peltier effect at the boundary and very small thermal inertia in addition to their large Seebeck coefficients and small thermal conductivities, they will be good materials in constructing mini-thermoelectric piles used for temperature difference monitoring in calorimetric system. In our own new developed adiabatic type calorimeter, such a miniature self-made device was used. It showed a sensitivity of $25\ \mu\text{V}$ per $0.001\ \text{K}$ change and an internal resistance of only $10\ \text{ohms}$.

3. Technical foundation for thermal compensation of heat effect accompanying the process within the calorimeter.

The processes or reactions are but "exothermic" and "endothermic" from the point of view of their accompanying heat effects. With the refrigeration technique by semiconductors electric energy can be converted directly to "heat" or "cool" to compensate either heat effect so that the heat effect can be determined accurately. In practice, it is only necessary to monitor the temperature differences between system and surroundings while maintaining the temperature of surroundings constant, and to control the compensation energy to the system according to the polarity and magnitude of monitoring signals. With the refrigeration technique by semiconductors, the energy density supplied is sufficient to the implementation of thermal compensation for the great majority of processes.

Based on the above considerations, we have

investigated the adaptability and applicability to calorimetry of the refrigeration technique by semiconductors, and developed a new versatile semiconductor calorimetric system.

II. EXPERIMENTAL

1. The Calorimetric System.

From the conceptions of system and surroundings, a calorimetric apparatus can be divided into two parts, the calorimetric unit and the thermostat. The calorimetric unit varies with different modes of measurements, but the thermostat may be a common one. In the light of this, the calorimetric units can be designed to be interchangeable for fitting into the same thermostat, so that calorimetric measurements of different modes will be accomplished in a calorimetric system with a common thermostat.

It should also be pointed out that since the requirements for the thermostat in the two traditional methods, the adiabatic and the isoperibol methods, are quite different, the use of a common thermostat is usually impossible. However, this problem can be easily solved if the refrigeration technique by semiconductors is adopted, and this has been confirmed in our work.

A calorimetric system (Model BD-1) with two interchangeable calorimetric units, the isoperibol and the adiabatic units, and a thermostat is described in the following (see Figs. 1 and 2).

As shown in Fig. 1, (1), (3), (4), (6), (9), (10), (11), (12), (13) and (14) constitute the thermostat compartment. It is about $10\ \text{dm}^3$ in volume and mainly consists of a cylindrical semiconductor thermoelectric pile, a vortex reaction type stirring system and an outer water jacket. The thermostat and the outer jacket are filled with water during experiment.

The cylindrical thermoelectric pile equipped to the thermostat was constructed with curved pieces of semiconductor thermoelectric elements jointed together by the #56 solder of our own developed BLH Solder Series. A technique for constructing it was developed by us. Considering that the thermoelectric pile would work at certain temperature differences, a flexible construction was designed to fit in with the thermal expansion of the materials. A similar piece of thermoelectric pile with less elements was tested for its per-

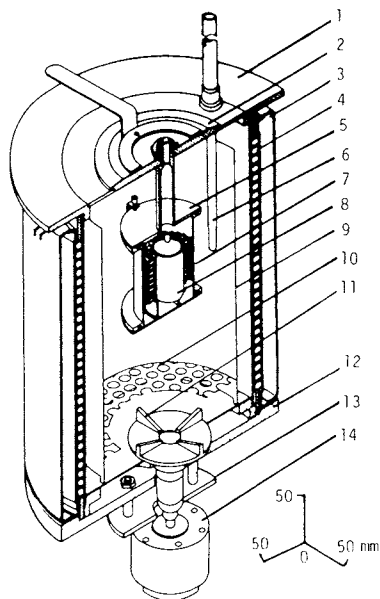


Fig. 1. Diagram of the Model BD-1 Calorimetric System for Solution Calorimetry.

(1) Cover of the thermostat, (2) support cover plate for the calorimetric unit, (3) outer water jacket, (4) semiconductor thermoelectric pile, (5) adiabatic jacket of the calorimetric unit, (6) Beckmann thermometer, (7) semiconductor thermoelectric sensor, (8) sample container, (9) reaction baffle shell, (10) perforated plate, (11) stirring propeller, (12) bottom of the thermostat, (13) support of electric motor, and (14) electric motor.

formances⁽³⁾ by applying current continuously to it for 2863 hours, and making it work repeatedly at temperatures ranging from -5 to 200°C . The results were satisfactory. For reducing the parasitic temperature differences, promoting the refrigeration efficiency and reducing the thermal lag, the plasma spray coating and other new thermal coupling techniques were adopted in constructing it.

The thermoelectric pile was designed to its maximum refrigerating capacity.⁽⁴⁾ It is composed of 1008 pairs of elements ($\phi 7 \times 8$ mm), and the p- and n-type materials are $\text{Bi}_2\text{Te}_3 \cdot \text{Sb}_2\text{Te}_3$ and $\text{Bi}_2\text{Te}_3 \cdot \text{Bi}_2\text{Se}_3$ with a figure of merit, Z , of $2.42 \times 10^{-3} \text{ K}^{-1}$. When operating at a temperature difference of 35 K, the thermoelectric pile has an effective refrigeration power of about 800 watts. Its internal resistance when not at work is 4.8Ω , or 6.7Ω while working at 5°C and 7.5Ω while at

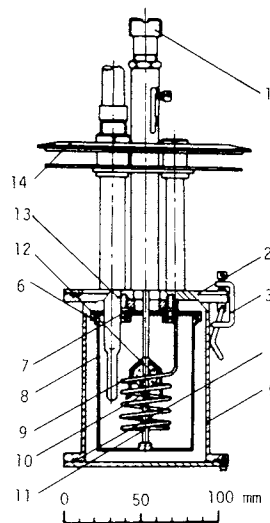


Fig. 2. A Diagram Showing the Construction of the Isoperibol Calorimetric Unit.

(1) Stirrer, (2) cover of air jacket, (3) movable clamp, (4) rubber o-ring for forming seal, (5) jacket well, (6) cover of calorimeter vessel, (7) Teflon bolt, (8) calorimeter vessel, (9) heater, (10) four-blade propeller, (11) "anvil" tapered to a point at the top for crushing the sample bulb, (12) glass sample bulb, (13) thermometer, and (14) support plate for the calorimetric unit.

25°C . Within the experimental temperature range, the power dissipation for raising or lowering the temperature is less than 140 watts, and less than 30 watts for temperature controlling. When in the working state of refrigerating or heating, the efficiency for the conversion of electric energy to heat can be 100 to 200%. The power supply is a dc constant-voltage power supply (Model WYZ-8).

The adiabatic calorimetric unit (see figure 1) is composed of a support cover plate for the calorimetric unit (2), the adiabatic jacket (5), which has highly polished chromium-plated brass walls and cover, and a rubber o-ring to form seal, a semiconductor thermoelectric sensor (7) for temperature difference monitoring with a sensitivity of $25 \mu\text{V}$ per mK, a gold-plated copper sample container of approximately 40 cm^3 (8) and a heater (approximately 124Ω) made of #42 BWG gauge, enamelled manganin wire passing non-inductively through a gold-plated copper capillary coil with leads soldered to the ends.

A diagram of the isoperibol calorimetric unit

is shown in Fig. 2.

2. Results of Measurements.

The specific heat capacity of water, c_p (298.15 K), obtained from measurements with the adiabatic calorimeter was $(4.176 \pm 0.013) \text{ JK}^{-1} \text{ g}^{-1}$ (Table 1).^{*} The enthalpy of solution of KCl, $\Delta_{\text{sol}}H(200 \text{ H}_2\text{O}, 298.15 \text{ K})$ obtained with the isoperibol calorimeter was $(17.56 \pm 0.01) \text{ kJ mol}^{-1}$ (Table 3). The results are in good agreement with the values recommended by the Physical Chemistry Division of IUPAC in 1974.

The electrical energy was measured with a dc potentiometer. In order to test the capability of the system for making measurements at temperatures below the ambient temperatures, we had measured the electrical energy equivalent of the adiabatic calorimeter, w , at 5.6°C and the enthalpy of solution of KCl at 5°C . The results were

$$w(278.75 \text{ K}) = (170.2 \pm 0.1) \text{ JK}^{-1} \text{ (Table 2),}$$

$$\text{and } \Delta_{\text{sol}}H(200 \text{ H}_2\text{O}, 278.15 \text{ K}) = (20.85 \pm 0.02) \text{ kJ mol}^{-1} \text{ (Table 4).}$$

The experimental precision is 0.07%. No comparisons with other values could be made for the enthalpy of solution of KCl in 200 H₂O at 5°C . From these measurements, it is, too, apparent that good results would be obtained with this isoperibol calorimeter at temperatures either below

or above the room temperatures.

III. CONCLUSIONS

We have discussed first the fundamental aspect of semiconductor calorimetry and put forward a few points for the design of calorimetric instruments. This proposition was proved through the development of a new versatile calorimetric system and some measurements with it. Several important points will be stated in the following.

(1) The idea of the adoption of the refrigeration technique by semiconductors in a calorimetric system in controlling temperature of surroundings was satisfactorily fulfilled. The semiconductor thermostat can be used either for adiabatic or for isoperibol mode of measurements. This makes possible to carry out the traditional calorimetric measurements of these two modes in one system with a common thermostat. Especially for adiabatic calorimetry, this thermostat has demonstrated the versatility in the ability to make precision measurements of slow or rapid reactions, either exothermic or endothermic. This is of great convenience for calorimetric measurements.

(2) The standpoint of dividing an actual calorimeter into two main parts, system and its surroundings, had led to the design of interchangeable

Table 1 The specific heat capacity, c_p , of water at $(25 \pm 0.01)^\circ\text{C}$.

| Expt. No. | Temp. rise $\Delta\theta$ K | Resistance of heater $\frac{R}{\Omega}$ | Elect. energy measured $\frac{Q}{\text{J}}$ | Elect. energy equivalent | | Specific heat capacity of water $\frac{c_p}{\text{JK}^{-1} \text{ g}^{-1}}$ |
|-----------|-----------------------------------|--|--|--|--|--|
| | | | | $\frac{w_1^{\text{a)}}}{\text{JK}^{-1}}$ | $\frac{w_1 - w_2^{\text{b)}}}{\text{JK}^{-1}}$ | |
| 1 | 1.299 | 123.456 | 260.10 | 200.23 | 20.27 | 4.1819 |
| 2 | 1.284 | 123.458 | 257.24 | 200.35 | 20.38 | 4.1861 |
| 3 | 1.285 | 123.454 | 257.33 | 200.25 | 20.29 | 4.1865 |
| 4 | 1.286 | 123.454 | 257.45 | 200.20 | 20.23 | 4.1743 |
| 5 | 1.287 | 123.454 | 257.52 | 200.09 | 20.13 | 4.1526 |
| 6 | 1.287 | 123.453 | 257.65 | 200.20 | 20.23 | 4.1743 |

$$c_p = (4.176 \pm 0.013) \text{ JK}^{-1} \text{ g}^{-1}$$

$$\sigma_{n-1} = \sqrt{\sum d_i^2 / (n-1)} = 0.0030$$

a) w_1 is the electrical energy equivalent of the first run of experiment with water sample.

b) w_2 is the electrical energy equivalent of the "empty" system that resulted by the removal of a measured amount of water from the system for which w_1 was determined.

* Uncertainties given in this paper are twice the standard deviations of mean, unless otherwise stated.

Table 2 Electrical energy equivalent of the adiabatic calorimeter (with water).

| Expt. No. | Temp. rise | Resistance of heater | Elect. energy measured | Elect. energy equivalent |
|-----------|---------------------------------|----------------------|------------------------|----------------------------|
| | $\frac{\Delta\theta}{\text{K}}$ | $\frac{R}{\Omega}$ | $\frac{Q}{\text{J}}$ | $\frac{w}{\text{JK}^{-1}}$ |
| 1 | 1.787 | 124.752 | 304.07 | 170.16 |
| 2 | 1.785 | 124.754 | 304.11 | 170.37 |
| 3 | 1.786 | 124.753 | 303.92 | 170.17 |
| 4 | 1.788 | 124.751 | 304.06 | 170.05 |
| 5 | 1.787 | 124.754 | 304.18 | 170.22 |
| 6 | 1.788 | 124.751 | 304.13 | 170.09 |

- (i) The mean resistance of the heater is $R = (124.7525 \pm 0.0018)\Omega$ and the relative error is $\epsilon = (\sigma_{n-1}/\bar{x}) \times 100 = 0.0014\%$, where \bar{x} is the arithmetic mean.
- (ii) The mean electrical energy equivalent is $w = (170.2 \pm 0.1) \text{JK}^{-1}$, and $\epsilon = 0.064\%$.

Table 3 Enthalpy of solution of KCl in 200 H₂O at (25±0.01)°C.

| Expt. No. | Energy equivalent measurements | | | | Resistance of heater | Enthalpy of solution measurements | | |
|-----------|--------------------------------|---------------------------------|------------------------------|----------------------|----------------------|-----------------------------------|---------------------------------------|--|
| | Elect. energy measured | Temp. rise | Elect. energy equivalent | Wt of KCl | | Temp. change | Enthalpy of solution | |
| | $\frac{Q}{\text{kJ}}$ | $\frac{\Delta\theta}{\text{K}}$ | $\frac{w}{\text{kJ K}^{-1}}$ | $\frac{W}{\text{g}}$ | | $\frac{\Delta\theta}{\text{K}}$ | $\frac{\Delta H}{\text{kJ mol}^{-1}}$ | |
| 1 | 1.22149 | 1.297 | 0.94178 | 352.237 | 4.3026 | 1.077 | 17.57 | |
| 2 | 1.17098 | 1.126 | 1.03995 | 352.232 | 4.7615 | 1.077 | 17.54 | |
| 3 | 1.33120 | 1.279 | 1.04081 | 352.228 | 4.7667 | 1.079 | 17.56 | |
| 4 | 1.10280 | 1.061 | 1.03940 | 352.303 | 4.7679 | 1.080 | 17.55 | |
| 5 | 1.13603 | 1.090 | 1.04223 | 352.227 | 4.7666 | 1.077 | 17.56 | |
| 6 | 1.09223 | 1.050 | 1.04022 | 352.227 | 4.7645 | 1.078 | 17.55 | |

$$\Delta_{\text{sol}}H(\text{KCl in } 200 \text{ H}_2\text{O, } 298.15 \text{ K}) = (17.56 \pm 0.01) \text{ kJ mol}^{-1}$$

Table 4 Enthalpy of solution of KCl in 200 H₂O at (5±0.01)°C.

| Expt. No. | Energy equivalent measurements | | | | Resistance of heater | Enthalpy of solution measurements | | |
|-----------|--------------------------------|---------------------------------|------------------------------|----------------------|----------------------|-----------------------------------|---------------------------------------|--|
| | Elect. energy measured | Temp. rise | Elect. energy equivalent | Wt. of KCl | | Temp. change | Enthalpy of solution | |
| | $\frac{Q}{\text{J}}$ | $\frac{\Delta\theta}{\text{K}}$ | $\frac{w}{\text{kJ K}^{-1}}$ | $\frac{W}{\text{g}}$ | | $\frac{\Delta\theta}{\text{K}}$ | $\frac{\Delta H}{\text{kJ mol}^{-1}}$ | |
| 1 | 1.06569 | 1.076 | 0.99044 | 351.868 | 4.6017 | 1.298 | 20.83 | |
| 2 | 1.06597 | 1.076 | 0.99069 | 351.871 | 4.6016 | 1.300 | 20.87 | |
| 3 | 1.06549 | 1.075 | 0.99161 | 351.870 | 4.6023 | 1.297 | 20.83 | |
| 4 | 1.06589 | 1.073 | 0.99337 | 351.867 | 4.6029 | 1.296 | 20.85 | |
| 5 | 1.06630 | 1.077 | 0.99006 | 351.877 | 4.6023 | 1.300 | 20.85 | |

$$\Delta_{\text{sol}}H(\text{KCl in } 200 \text{ H}_2\text{O, } 278.15 \text{ K}) = (20.85 \pm 0.02) \text{ kJ mol}^{-1}$$

calorimetric units, and thus to the success in constructing a versatile calorimetric system suitable for making precision measurements of different heat effects in different modes. The refrigeration technique by semiconductors facilitated the construction.

It is difficult in general to carry out measurements in adiabatic and isoperibol modes with a common thermostat in traditional calorimetric methods because the heat effects are various. The practice in this work had simplified and solved many of these complex problems.

(3) Sensors made of the mentioned semiconductor materials for temperature difference monitoring in calorimetry are highly sensitive, as were expected from discussing the characteristics of the materials. Satisfactory results were obtained with the sensor equipped in the adiabatic calorimetric unit and surely will be obtained if they are adopted in other calorimetric methods such as in conduction microcalorimetry.

(4) From the practice with this versatile semiconductor calorimetric system, it can be expected that the realization of the compensation mode of calorimetric measurements will be entirely possible. The technology for constructing cylindrical thermoelectric pile with curved pieces of elements would also be appropriate and adaptable for this purpose.

(5) The present semiconductor thermostat is able to operate in a temperature range from 0 to 60°C.

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