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PRINCIPLE AND EXPERIMENTAL VERIFICATION OF COMPENSATION CALORIMETRY *

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ABSTRACT

A new principle of calorimetry, i.e., the principle of compensation calorimetry, is proposed on the basis of modern electronic technology and computer science: its main points are introduced. A prototype of a "digital compensation calorimeter" has been designed and built following the new principle. Elementary verification of the new principle has been obtained through experiments for calibration of the prototype's "pulse energy equivalent" and for the measurement of stirring heat.

GENERAL REVIEW

It is not a new concept in calorimetry to measure heat effect with compensation methods. The ice-calorimeter of many years ago, for instance, was using ice dissolution heat to compensate for exothermic processes. In micro-calorimetry, electric energy is used to compensate for heat effects. The ice-calorimeter is not widely used because, beside its complex structure, it fails in measuring heat effects of endothermic processes, and the phase transition temperature strongly narrows its application. Local compensation of a heat effect is the basic method in micro-calorimetry, but its application is almost confined within that field.

The development of modern electronics makes it possible to measure various heat effects with the heat compensation method. Much work has been done since the 1960s on calorimetry using compensation methods with the semiconductor refrigerating technique. J.J. Christensen et al. have made outstanding contributions in their research work from 1968 [1] to 1981 [2]. On the basis of the semiconductor refrigerating technique, they have mea-

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sured heat effects with current pulses by thermal compensation through adjustable Joule heating and constant Peltier refrigerating.

Christensen's calorimeter, with improvements and modifications later on, has been adopted by Tronac as a commercial product, in which there are two patented techniques [3], viz., the semiconductor refrigerating pile and the electric pulse heating controller for the thermostat.

The heat effect under test is compensated while measuring with this kind of calorimeter, so that the system temperature e is kept unchanged or, $\Delta e = 0$, during the whole measurement period. The heat effect is balanced with electrical energy applied in the form of current pulses from which the magnitude of the heat effect is determined. It is seen that there is almost no heat exchange between the system and the environment so that there is no need to determine the calorific equivalent of the calorimeter as we have to with the conventional method. Though similar to traditional isothermal calorimetry, the compensation method is distinct from the classical ones both in principle and implementation. Other researchers than Christensen have made their contributions in this field, but his is the most outstanding and systematic.

Although much work has been done on measuring the heat effect through thermal compensation with the semiconductor refrigerating technique, systematic and theoretical research on thermal compensation technology has not yet been reported. To further develop and improve this promising technology, we propose in this paper a model of compensation calorimetry on the basis of semiconductor refrigeration and digital process control with micro-computers.

INTRODUCTION TO COMPENSATION CALORIMETRY

The main points of the principle are as follows:

(1) The calorimeter is a device in which an unknown heat effect is compensated or balanced with known quantities of electric energy. The system temperature is kept unchanged during the whole period of measurement. The electrical energy consumed for compensation is equivalent to the energy of the heat effect to be determined.

(2) An exothermic process makes the system temperature go up while an endothermic one makes it go down, if the process takes place in an adiabatic environment. Either process can be described with a temperature–time function curve. In compensation calorimetry, measurement of the heat effect is realized by providing a temperature–time curve that is the same in magnitude as but opposite in polarity to the curve of the heat effect under test. This is referred to as a compensation curve.

(3) The processes or reactions are either exothermic or endothermic from the point of view of the accompanying heat effects. With the refrigeration

technique by semiconductors, electrical energy can be converted directly into "heat" or "cold" in order to compensate either kind of heat effect. The energy density provided by the semiconductor refrigerating pile is sufficient to implement thermal compensation for the great majority of processes. That is to say, the semiconductor refrigerating technique is able to provide the compensation energy required in compensation calorimetry.

(4) Mathematically speaking, a continuous function curve can be represented with a number of concrete points if the sampling interval is small enough. It is well known that an electrical pulse carries certain energy and pulse counting is simple and accurate. The compensation curve can be represented by a sequence of pulse strings in which each string represents a concrete point of the compensation curve. The energy introduced into the calorimetric system by one electric pulse can be calibrated with accuracy and the calibrated value is referred to as "pulse energy equivalent". It is seen that the magnitude of compensation energy is the product of pulse count and pulse energy equivalent.

(5) The semiconductor refrigerating technique, combined with pulse circuits, meets the necessary requirement of providing the compensation function curve. To make it sufficient, the curve provided must be as described in (2), that is, "the same in magnitude as but opposite in polarity to" that of the heat effect under test. A calorimeter, no matter what kind it is, consists of two parts, i.e., the system and the environment. Suppose that the temperature of the environment is kept unchanged during the whole measurement period, then the polarity and magnitude of the compensation energy are dependent upon the polarity and magnitude of the temperature difference between the system and the environment, while the difference is proportional to the energy of the heat effect that takes place in the system. The temperature difference signal can be V/F converted into pulse frequency from which the compensation pulse sequence is determined and fed into the system to equalize the difference. Whenever any temperature difference appears between the system and the environment as the heat effect varies, a corresponding pulse sequence will be generated and applied accordingly. This process is repeated until the end of the heat effect.

(6) Compensation calorimetry requires that the heat power derived from the compensation function curve should be, at any moment of measurement, the same in magnitude as that generated by the heat effect under test: theoretically speaking, they should balance each other exactly. It is seen that such a technique must be automatic. To a certain extent, an automatic adjuster is simply a feedback system, and the compensation calorimeter can be viewed as a heat feedback system that compensates the heat effect under test. It is seen from the above description that such a system is a negative feedback one with its feedback coefficient $B = 1$.

(7) A block diagram of the compensation calorimeter is shown in Fig. 1. Both system and environment are kept at the same preset temperature

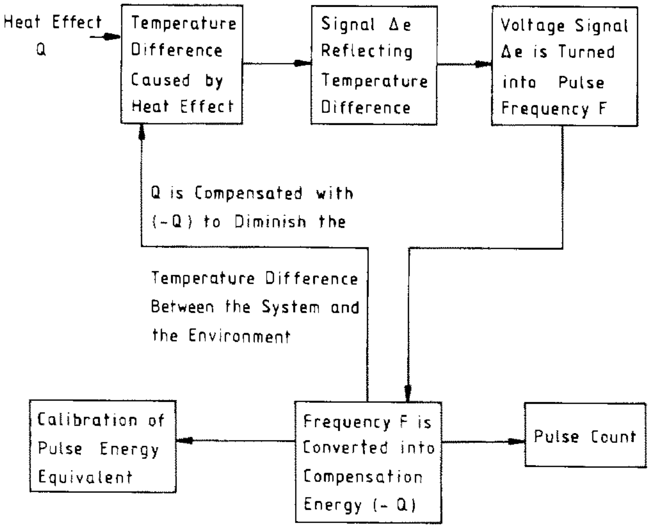

Fig. 1. Block diagram of the compensation calorimeter.

before the main period of measurement and the temperature of the environment is kept unchanged throughout the whole period of measurement. There is a temperature difference between the system and the environment during the main period (after the heat effect under test takes place). The compensation pulse sequence is derived from the temperature difference and applied to the compensation pile in order to make the system return to its original temperature. This feedback process is repeated during the whole period of measurement until the end of the heat effect.

It is to be pointed out that the heat energy feedback should be taken as the result of information transmission and information interaction. The appearance of a temperature difference generates a signal Δe, i.e., there is heat effect taking place in the system. The signal is fed into and processed by the automatic adjuster, where it is turned into compensation energy which is the same in magnitude as but is opposite in polarity to the energy of the heat effect. The compensation energy is applied to the system and balanced with its opponent, making Δe disappear, so as to complete a compensation cycle. During the measuring process, the heat effect does not appear as output from the system but, on the contrary, it is compensated or balanced, with this compensation realized through information feedback.

VERIFICATION OF THE PRINCIPLE

A prototype "digital compensation calorimeter" was designed and built following the principle described above. A micro-computer controlled semiconductor thermostat is used for the prototype's environment temperature control. The temperature control precision is as high as $e \pm 0.0001\,^\circ\mathrm{C}/24$ hour at any given temperature from 5 to 60 °C [4]. The thermostat meets the necessary requirement of the principle, that is, the temperature of the environment should be kept unchanged throughout the measurement period. A temperature difference sensor with low internal resistance is placed between the system and the environment. Its sensitivity is $\pm 0.001\,^\circ\mathrm{C}$, one order less than that of the temperature control precision. It is so arranged that the temperature difference signal Δe is proportional only to the heat effect taking place in the system, without being interfered with by drift of the environment temperature. The analog signal Δe is A/D converted and then fed into and processed by a micro-computer, from which the compensation pulse sequence is derived and applied to the system through the compensation pile [5]. The measurement result is directly displayed in digital form on the micro-computer's screen.

The digital compensation calorimeter and the measurement of the dissolution heat of KCl and NaCl in water will be expounded elsewhere. Here we introduce only the calibration of "pulse energy equivalent" and the measurement of stirring heat.

Selection of working waveform of compensation pile

In our experiment, pulse waveform is chosen as shown in Fig. 2. The pulse width is 1 ms while its amplitude is 40 V. As shown in Fig. 2, the compensation pulse frequency is 500 Hz, corresponding to the largest compensation power.

Frequency modulation is implemented by adjusting the pulse period T with pulse width being constant, as shown in Fig. 3. The compensation pile

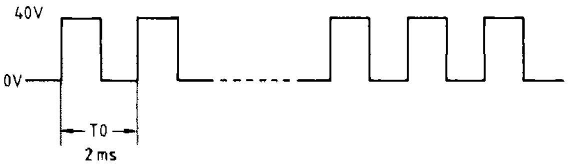

Fig. 2. Pulse waveform for the largest compensation power.

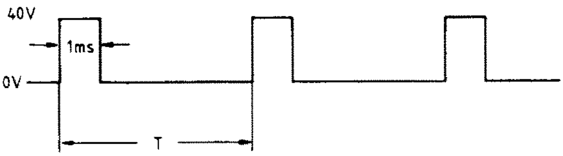

Fig. 3. Pulse waveform for normal compensation power.

and its associated circuit are so designed that the compensation power provided is sufficient for any heat effect taking place in the measuring unit, i.e., the pulse period T during normal compensation is always longer than or equal to T_0. Actually, T is proportional to the temperature difference signal Δe and may vary from time to time. But the pulse width is kept strictly unchanged during measurement. That is to say, the pulse frequency, or the number of pulses applied within a compensation cycle, may only vary while the pulse energy equivalent remains constant.

One compensation cycle of the prototype is 0.5 s in which there may be 250 pulses at most, corresponding to the largest compensation power. For the least non-zero compensation power, there is only one pulse.

Calibration of pulse energy equivalent

Compensation function curve

The experiment is carried out at 25 °C. The measuring unit is filled with a certain amount of water or other liquid. The unit is sealed and put into the thermostat. The temperature control program is initiated and the thermostat temperature is automatically controlled at 25 ± 0.0001 °C for about 30 minutes. The compensation program is then started and the system temperature is automatically kept to the same as that of the thermostat. This is indicated by the temperature difference signal $\Delta e = 0$. Meantime electrical energy is applied to the system, and a compensation function curve shown in Fig. 4 is obtained through observation of the temperature difference signal Δe.

Curves 1 and 2 in Fig. 4 correspond to two compensation processes, the electrical power for each being 0.06 and 0.01 cal s^{-1}, respectively. It is seen

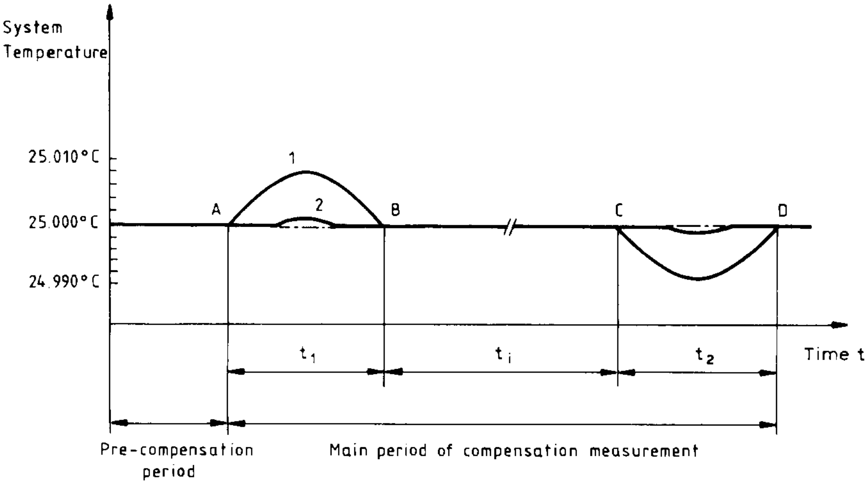

Fig. 4. The compensation function curve.

from Fig. 4 that there are three stages in a compensation process. The first stage, before point A, is the stage of system temperature adjustment, in which pulses are applied to the system through the compensation pile so as to make the system temperature the same as that of the environment, that is, $\Delta e = 0$. The second stage, from point A to B, labeled by t_1, is called the "pre-compensation period", in which electrical energy is applied to the system and the compensation process commences. It is seen from the description of our principle that the compensation energy applied in this stage should be in the form of "coldness" against the Joule heat generated by the electrical energy. If the electrical energy is large, the system temperature may deviate from its equilibrium point because of incomplete compensation at the very beginning of t_1 when electrical power is first applied. The temperature deviation lasts only a few seconds. As shown in Fig. 4, there is a temperature offset of at most $+0.008\,^\circ\mathrm{C}$ from point A to B. From point B on, the system temperature follows the environment temperature exactly and a "complete compensation period" takes place. The "post-compensation period" t_2 begins from point C when the electrical power is turned off. Again a system temperature deviation is seen of the same amplitude as in t_1 but of opposite polarity, i.e., $-0.008\,^\circ\mathrm{C}$. The measurement accuracy is not affected significantly, because the system temperature deviations in the periods t_1 and t_2 are small, short and precisely symmetric.

It takes time for the compensation program to follow the heat effect of large heat power, which is the main cause of the system offsets in t_1 and t_2. Both amplitude and duration decrease for heat effects of small heat power, such as curve 2 in Fig. 4. Its offsets are only $0.002\,^\circ\mathrm{C}$ in amplitude. There will be no offsets at all if the electrical power applied is less than 0.01 cal s^{-1}. All in all, the system temperature effectively follows environment temperature throughout the whole measurement period. The compensation function curve and the curve of the heat effect under test are "the same in magnitude as but opposite in polarity to" each other, just as required in (2) of our principle. The compensation pulses are counted, recorded and displayed by the prototype's micro-computer. The pulse energy equivalent is thus calibrated from the pulse count and the electrical energy applied into the system.

Calibration results

It is seen from the description in (4) of the principle that "the energy carried by an electrical pulse can be calibrated with accuracy and, the calibrated value is referred to as pulse energy equivalent". The process for calibration of pulse energy equivalent against known electrical energy is shown in Fig. 4. In Table 1 are listed the original data of a calibration experiment, and in Table 2, the result of data processing for the same experiment.

TABLE 1

Calibration of pulse energy equivalent

No.	t_i	t_0 (s)	P_1	P_2	P_3	P'_0	e_p (mv)	e_n (mv)	V_r (V)	V_h (V)
1	522	137.856	26035	234	25801	94	0.27	0.27	4.512	5.817
2	482	124.427	23641	124	23517	96	0.27	0.27	4.516	5.822
3	499	127.923	24424	159	24265	96	0.27	0.26	4.519	5.825
4	524	123.767	23692	44	23648	96	0.27	0.28	4.523	5.831
5	505	127.685	24586	83	24503	96	0.27	0.27	4.523	5.832
6	484	124.371	23841	156	23685	96	0.26	0.28	4.524	5.832
7	502	124.540	24040	124	23916	96	0.27	0.27	4.525	5.834
8	500	122.177	23506	126	23380	95	0.27	0.26	4.525	5.834
9	485	123.527	23586	167	23419	96	0.27	0.27	4.525	5.833
10	471	117.472	22518	20	22498	96	0.28	0.27	4.525	5.834
11	502	121.597	23149	123	23026	96	0.28	0.27	4.525	5.834
12	495	125.815	24125	143	23982	100	0.28	0.27	4.527	5.836

No., experiment sequence number; t_i, the number of compensation cycles; t_0, duration time when electrical energy is applied; P_1, pulse count when the pile is refrigerating; P_2, pulse count when the pile is heating; P_3, pure count, the algebraic sum of P_1 and P_2; P'_0, compensation power while the electrical energy is on and $\Delta e = 0.00$ mv; e_p, maximum positive deviation of system temperature; e_n, maximum negative deviation of system temperature; V_r, voltage drop across the standard resistor; V_h, voltage drop across the heater.

TABLE 2

Example of data processing for experimental results

No.	I_h (A)	R_h (Ω)	Q (cal)	Q_0	P_3	$W\times10^4$ (cal pulse^{-1})
1	0.04512	128.92	8.6479	1566	24235	3.568
2	0.04516	128.92	7.8191	1446	22071	3.543
3	0.04519	128.90	8.0482	1497	22768	3.535
4	0.04523	128.92	7.8017	1572	22076	3.534
5	0.04523	128.94	8.0501	1515	22988	3.502
6	0.04524	128.91	7.8429	1452	22233	3.528
7	0.04525	128.93	7.8580	1506	22410	3.506
8	0.04525	128.93	7.7089	1500	21880	3.523
9	0.04525	128.91	7.7927	1455	21964	3.548
10	0.04525	128.93	7.4120	1413	21085	3.515
11	0.04525	128.93	7.6723	1506	21520	3.565
12	0.04527	128.92	7.9446	1485	22497	3.531

No. and P_3 are the same as in Table 1; I_h, heater current; R_h, heater resistance; Q, electrical energy applied to the system; Q_0, pulse count for stirring heat; W, magnitude of pulse energy equivalent.

Pulse energy equivalent is calculated as follows

$$W = Q/P_3$$

The calculation result was

$$W = 3.533\times10^{-4}\ \text{cal} = 0.35\ \text{mcal}$$

$$\sigma_{n-1} = \pm0.021\times10^{-4}\ \text{cal} = \pm0.002\ \text{mcal}$$

In Table 1, P_1 is the sum of pulses applied into the system when the compensation pile is refrigerating, P_2 is that when the pile is heating and P_3, the pure count, is the algebraic sum of P_1 and P_2. Either exothermic or endothermic processes can be measured with accuracy by the three parameters. P_0 is the number of pulses in the current compensation cycle; $P_0\times2$ represents the compensation power, because one compensation cycle is exactly 0.5 second. For a heat effect with constant heat power, $2P_0\times t_i$ gives the magnitude of its total heat energy, where t_i is the number of compensation cycles. For a heat effect with variable heat power, P_0 varies accordingly.

The results of measuring stirring heat are given in Table 3. They are obtained from "blank experiments". A certain amount of liquid is introduced into the measuring unit and no heat effect takes place there except for the stirring heat. Twenty-two experiments were made in two groups: one of them is listed in Table 3.

Measurement of the stirring heat

$$Q_0 = 1322$$

$$\sigma_{n-1} = 79$$

TABLE 3

Measurement of stirring heat

No.	t_i (s)	P_1	P_2	P_3	P_0'	Q_s (cal)
1	550	1578	0000	1578	3	0.558
2	550	1540	0000	1540	3	0.544
3	550	1568	0000	1568	3	0.554
4	550	1731	0000	1731	3	0.612
5	550	1510	0000	1510	3	0.533
6	550	1631	0000	1631	4	0.576
7	550	1747	0000	1747	2	0.617
8	550	1741	0000	1741	3	0.615
9	550	1566	0000	1566	3	0.553
10	550	1825	0000	1825	3	0.645
11	550	1451	0000	1451	3	0.513

No., t_i, P_1, P_2, P_3 and P_0' are the same as in Table 1; Q_s is the magnitude of stirring heat within 275 s.

Stirring heat power

$P_0 = 1322/450 = 2.94$ pulse $(0.5 \text{ sec})^{-1}$

According to the equivalent found in Table 2, we have

$P_0 = 5.88 \times 0.35 = 2.1 \text{ mcal s}^{-1}$

Therefore, stirring heat in 225 seconds will be

$Q_0 = 2.1 \times 225 = 472.5$ mcal

Stirring heat for another group is

$t_i = 550 = 275$ s, $n = 11$, $Q_0 = 1670$, $\sigma_{n-1} = 118$

$P_0 = 2.96$ pulse $(0.5 \text{ s})^{-1} = 5.92$ pulse s^{-1}

The two results of P_0 coincide with each other up to a repeatability of 0.7%.

TABLE 4

Measurement of pulse energy equivalent

No.	Number of meas.	Elec. power (cal s^{-1})	Pulse energy equivalent W (mcal)	Standard deviation σ_{n-1} (mcal)
1	12	0.2619	0.3343	0.0012
2	11	0.2081	0.3362	0.0034
3	12	0.1165	0.3405	0.0048
4	12	0.0509	0.3447	0.016
5	12	0.0290	0.3618	0.018

Experiments for calibration of pulse energy equivalent are also carried out with the measuring unit being filled with 20 or 30 g of pure water or NaCl solution. The measuring time and electric heat power are also varied in those experiments (Table 4). Experiments for measuring the dissolution heat of KCl and NaCl in water will be found in another paper. All of the results show that pulse energy equivalent is independent of the material used in the measuring unit as well as the duration of the heat effect under test, which verifies the correctness of the principle proposed herein.

CONCLUSIONS

The process of calibrating pulse energy equivalent is in fact the process of compensating the exothermic heat effect. The prototype's stirring heat is measured with the calibrated equivalent. Complete compensation is obtained for heat effects with heat power less than 0.01 cal s^{-1}. These facts prove the correctness of points (1), (2) and (6) of the principle.

Points (3), (4) and (5) of the principle are also proved from the experimental results, that is

(a) A special semiconductor refrigerating pile is used for providing compensation energy, with the pile under the control of a micro-computer. Depending on the polarity of the temperature difference Δe, the pile is "refrigerating" or "heating". Experimental results for compensation of the endothermic process, for which the dissolution heats of KCl and NaCl in water are chosen, will be found in another paper of ours.

(b) Compensation energy is applied to the system in the form of electrical pulses. Experimental results show good repeatability for the calibration of pulse energy equivalent, which proves point (4) of our principle.

(c) The temperature difference signal Δe is V/F converted into a compensation pulse sequence and applied to the pile as compensation energy under the control of the micro-computer. The number of compensation cycles t_i is listed in Table 1. All this shows that point (5) of the principle is valid.

Verification of the principle in this paper is in the early stages, and more work should be done on both the principle and implementation of compensation calorimetry. Further research work in this field will be found in the paper entitled "Digital Compensation Calorimeter" (to be published).

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