

$$\begin{aligned} \text{Amp}(T_s(t)) &= \left| 2f \cdot \int_{-1/2f}^{+1/2f} (T_s(t+t') - \overline{T_s}(t+t') \cdot \exp(-i \cdot 2\pi f t')) dt' \right| & (1) \\ \text{Amp}(q_s(t)) &= \left| 2f \cdot \int_{-1/2f}^{+1/2f} (q_s(t+t') - \overline{q_s}(t+t') \cdot \exp(-i \cdot 2\pi f t')) dt' \right| & (2) \\ \text{Amp}(q_r(t)) &= \left| 2f \cdot \int_{-1/2f}^{+1/2f} (q_r(t+t') - \overline{q_r}(t+t') \cdot \exp(-i \cdot 2\pi f t')) dt' \right| & (3) \end{aligned}$$

where Amp ( ) indicates the AC amplitude of the signal inside the parentheses, | | indicates the absolute value of the value enclosed thereby, exp ( ) indicates an exponential function, or a function expressing the index of the value included in the parentheses,  $i$  is the imaginary unit  $(-1)^{1/2}$ , and  $\pi$  is the ratio of the circumference of a circle to its diameter.

By using a calculation method similar to the method used in AC calorimeters, the difference  $\Delta C_p$  (mJ/°C.) in AC heat capacity between the unknown sample and the reference sample is found from the AC amplitudes of the signals as follows.

$$\Delta C_p = \frac{\text{Amp}(q_s) - \text{Amp}(q_r)}{2\pi f \cdot \text{Amp}(T_s)} \quad (4)$$

Especially, where the operator performs a measurement in such a way that the container for the reference sample is empty the above  $\Delta C_p$  indicates the AC heat capacity of the unknown sample itself. As is well known in the field of AC calorimeters, the AC heat capacity of an unknown sample does not indicate a latent heat associated with a transition caused by the unknown sample. The above  $\Delta C_p$  signal is also supplied to plotter 17 from processor 16.

Thus, processor 16 derives an indication of the heat capacity of the unknown sample according to a ratio of a difference between the AC amplitude of the output signal from converter 13 and the AC amplitude of the output signal from converter 14 to the AC amplitude of the output from converter 15.

The above differential heat capacity  $\Delta C_p$  can be transformed into units of heat flow which can be compared with the above-described total heat flow component signal, by multiplying  $\Delta C_p$  by the average temperature rise rate  $d\overline{T_s}/dt$  of the unknown sample. That is, the heat capacity component ( $C_p$  component) is defined by the following equation:

$$C_p \text{ component (mW)} = -\Delta C_p (\text{mJ/}^\circ\text{C.}) \times \frac{d\overline{T_s}}{dt} \quad (^\circ\text{C./s}) \quad (5)$$

Thus, since  $\Delta C_p$  constitutes an indication of the heat capacity of the unknown sample itself, processor 16 provides an indication in units of heat flow as a signal,  $C_p$  component, indicative of the heat capacity component based on  $\Delta C_p$  multiplied by the average temperature change rate of the low frequency component of the output signal from converter 15.

The heat capacity component obtained in this way is not affected by the latent heat produced by a transition or reaction produced by or in the unknown sample and, therefore, this component acts to give the baseline when the latent heat is found from the DSC signal. This component is calculated by processor 16 and sent to plotter 17. The

difference between the above-described total heat flow component signal " $q_s$ "-" $q_r$ " and the above heat capacity component reflects only the latent heat component. This is defined as the kinetic component signal according to the following equation:

$$\text{kinetic component (mW)} = \text{total heat flow component (mW)} - \text{total heat capacity component (mW)}$$

Thus, the kinetic component signal is based on a difference between the value of the total heat flow component signal and the value of the signal indicative of a component of the heat capacity.

The kinetic component obtained in this way is also supplied to plotter 17 from processor 16.

Various signals including the total heat flow component signal, the heat capacity component signal, and the kinetic component signal delivered from processor 16 as described above are recorded on plotter 17 with respect to either the average temperature " $T_s$ " of the unknown sample, taken over one period, or time.

In the present example, thermocouples are used in measuring the temperature differences  $\Delta T_s$  and  $\Delta T_r$ . Commercially available thermomodules and platinum resistors can also be employed.

Of course, if a refrigerant such as liquid nitrogen, vaporized refrigerant, or other cooling means is used in conjunction with heater 4, then the response of the control over the temperature in heat reservoir 1 is effectively improved.

In order to investigate the thermal property of an unknown sample, the temperature difference  $\Delta T_s$  between thermocouple junction 9 on the side of the unknown sample and thermocouple junction 11 connected to heat conduction plate 6 is found while measuring the temperature difference  $\Delta T_r$  between thermocouple junction 10 on reference sample support portion 6b and the thermocouple junction 12 on heat conduction plate 6. The difference between these differences  $\Delta T_r$  and  $\Delta T_s$  is found. Thus, the heat capacity and the latent heat of the unknown sample are determined. If the temperature elevation conditions and reference sample support portion 6b remain the same, then the change in  $\Delta T_r$  with respect to time or temperature is maintained constant. Consequently, the above-described measurement object can be accomplished simply by measuring the temperature difference  $\Delta T_s$ .

As described thus far, in the present invention, a heat flux type DSC is so improved that a heat flow on the side of an unknown sample and a heat flow on the side of a reference sample can be measured independently and that the temperature of a heat reservoir can be controlled according to a ramp function modulated with an alternating sinusoidal wave. In consequence, DSC measurements can be performed. Additionally, the AC heat capacity of the unknown sample can be measured with high accuracy. Also, only information about the heat capacity can be extracted from a DSC signal which inevitably includes information about the latent heat, as well as information about the heat capacity. Hence, the baseline of the DSC signal becomes apparent. The latent heat of the unknown sample can be measured accurately. Further, with respect to a complex DSC thermogram, the instrument itself judges whether a change in the DSC signal is caused by a change in the heat capacity of the unknown sample or by a latent heat. Therefore, when data is interpreted, the possibility of human errors is reduced drastically.

This application relates to subject matter disclosed in Japanese Application number 5-238408, filed on Sep. 24, 1993, the disclosure of which is incorporated herein by reference.