

In considering heat effects upon the differential couple, the equations of heat balance employed by Borchardt and Daniels are used (5).

$$C_{p,s}dT_2 = dH + K_s(T_3 - T_2)dt \quad (1)$$

$$C_{p,r}dT_1 = K_r(T_3 - T_1)dt \quad (2)$$

T_1 , T_2 , and T_3 are temperatures of the reference thermocouple, sample thermocouple, and air bath (furnace thermocouple), respectively (see Figure 1). $C_{p,r}$ is the total heat capacity of the reference thermocouple (including cup) and $C_{p,s}$ is the total heat capacity of the measuring thermocouple including cup. The absolute values which will be obtained are dependent upon the effects of thermocouple symmetry, size, and shape of sample containers and furnace, when these variables can be reduced to constants as in a fixed system.

Equation 1 shows that any increase in enthalpy of the sample side of the differential thermocouple is due to the total enthalpic effects of sample plus the heat transferred to the thermocouple by the surroundings. Equation 2 describes the enthalpic effects on the reference side except that the dH term is necessarily not present. K_s is the heat transfer coefficient for the sample (measuring) thermocouple and K_r is the heat transfer coefficient for the reference side.

The assumptions governing the validity of these equations to the present system are: the differential thermocouples are fixed; a small sample size is employed; the sample does not have to be diluted; the sample holder is capable of maintaining even heat distribution consistent with the demands of the temperature programmer; and linear heating rates from one run to the next can be realized.

There are two situations which we must consider—the absence of a sample and the presence of a sample. Let us consider the first case where a sample is not present in the container. In this instance there can be no heat evolution or absorption except that due to slightly different heat capacities of the thermocouples and empty containers caused by symmetry and size considerations.

Then, any change in base line from the horizontal due to differences in heat capacity may be expressed as:

$$C_{p,s}dT_2 - C_{p,r}dT_1 = K_s(T_3 - T_2)dt - K_r(T_3 - T_1)dt \quad (3)$$

where $C_{p,s}dT_2 - C_{p,r}dT_1 = C_p dT$ and C_p = heat capacity of the system. K_r and K_s , the heat transfer coefficients from T_3 to T_2 and T_3 to T_1 , should be equal even under dynamic conditions providing linear reproducible programming rates exist, thermal gradients within the holder are absent, and the total

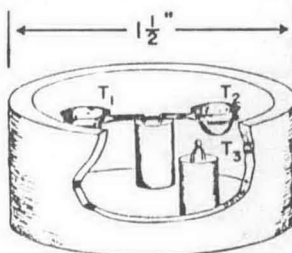


Figure 1. Sample holder

T_1 = Reference temperature
 T_2 = Sample temperature
 T_3 = Air bath temperature

heat capacity of the air bath is more than sufficient to provide the thermal energy required to maintain nearly equilibrium conditions within the system.

Rearranging Equation 3 gives

$$C_p dT = K(T_1 - T_2)dt \quad (4)$$

where $K = K_r = K_s \neq 0$

This is true providing the previous assumptions are true and K_r and K_s are temperature independent over the temperature range of interest (dT). This is indeed true as will be shown later.

Thus Equation 4 becomes

$$C_{p(w/o \text{ sample})} = \frac{K(T_1 - T_2)dt}{dT} = \text{cal./}^\circ\text{C.} \quad (5)$$

where

K = heat transfer coefficient of system in cal./mm.².

C_p = heat capacity of system in cal./°C.

dT = temperature range of interest

$(T_1 - T_2)dt = \Delta T dt$; and over a time interval, say t_0

$\int_t^{t_0} \Delta T dt$ = area encompassed by base line curve and constructed horizontally, measured over temperature range of interest.

The K value does not incorporate a time-temperature function since the chart speed of the recorder and the response of the DC amplifier and recorder were considered fixed.

We now consider the second case where a sample has been placed in the proper container and the enthalpic effects will be registered on T_2 which is one side of the differential couple.

We now choose a time (temperature) interval where $dH = 0$ —i.e., the heat of transformation is 0 because the sample is not undergoing a chemical or physical transformation. Thus, the equation

describing the heat capacity due to the presence of a sample is identical to Equation 5. By evaluating Equation 5 without sample and subsequently with sample and subtracting, the heat capacity of the sample is

$$\bar{C}_p = C_{p(w/o \text{ sample})} - C_{p(w/sample)} = (\text{System effects}) - (\text{System} + \text{sample effects}) \quad (6)$$

$$= \frac{K \Delta T dt}{dT} (w/o \text{ sample}) - \frac{K \Delta T dt}{dT} (w/sample) \\ = \frac{K}{dT} (\Delta T dt)_{\text{area due to sample}} \quad (7)$$

But there are thermal effects within the sample. Through the sample itself a thermal lag occurs and the rate at which heat is received by the measuring side of the differential couple becomes highly dependent upon sample size, heating rate, and the thermal diffusivity (α) of the sample. The lag experienced is precisely why the specific heat can be measured since it is characteristic of each material.

Therefore, we must take into account, thermal effects within the sample and consider the diffusion effects by means of the following equation (10, 16, 32).

$$\frac{dT}{dt} = \frac{k}{\rho C_p} \frac{d^2T}{dx^2} \quad (8)$$

where

$\frac{dT}{dt}$ = change of temperature of sample with respect to time

k = thermal conductivity of sample

ρ = density of sample

C_p = specific heat of sample

$\frac{d^2T}{dx^2}$ = rate of change of the temperature through the sample

The average heat capacity of the sample can now be defined by solving for C_p in Equation 8 and adding to Equation 7.

$$\bar{C}_p = K \Delta T \frac{dt}{dT} + \frac{k}{\rho} \left(\frac{d^2T}{dx^2} \right) \frac{dt}{dT} \quad (9)$$

= (sample effects) + (sample thermal diffusivity effects)

$$= \left(\rho + \frac{k}{\Delta T K} \frac{d^2T}{dx^2} \right) \Delta T dt \frac{K}{\rho dT} \quad (10)$$

Allowing for sample size Equation 10 becomes

$$\bar{C}_p = \frac{K' K (\Delta T dt)_{\text{area due to sample}}}{\rho g dT} \quad (11)$$

which describes the average specific heat of the sample.