# Chapter 5. Calorimetiric Properties

(1) Specific and molar heat capacities

(2) Latent heats of crystallization or fusion

A. Heat Capacity

- The specific heat capacity is the heat which must be added per kg of a substance to raise the temperature by one degree

1. Specific heat capacity at const. Volume

$$c_v = \left( \frac{\partial U}{\partial T} \right)_v \qquad (J/kg \cdot K)$$

2. Specific heat capacity at cont. pressure

$$c_p = \left( \frac{\partial H}{\partial T} \right)_p \qquad (J/kg \cdot K)$$

3. molar heat capacity at constant volume

$$\mathbf{C}_v = \mathbf{M}_{cv} \quad (J/mol \cdot K)$$

4. molar heat capacity at constat pressure

$$\mathbf{C}_p = \mathbf{M}_{cp} = \left( \frac{\partial H}{\partial T} \right)_p \qquad (J/mol \cdot K)$$

Where **H** is the enthalpy per mol

∘ Molar heat capacity of solid and liquid at 25℃

- Table 5.1 (p.111)에 각각 group 의 $C_p^s$(Satoh)와 $C_p^l$(Show)에 대한 data 를 나타내었다.
- Table 5.2 (p.112,113)에 각 polymer 에 대한 $C_p^l, C_p^s$ 값들을 나타내었다.
- (Ex 5.1)에 polypropylene 의 $C_p$를 구하는 것을 나타내었다.
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∘ Specific heat as a function of temperature

- 그림 5.1 에 polypropylene 의 molar heat capacity 에 대한 그림을 나타내었다.

◦ The slopes of the heat capacity for solid polymer

$$\frac{1}{C_p^{\ s}(298)}\frac{dC_p^{\ s}}{dt}=3\times10^{-3}$$

$$\frac{1}{C_p^{\ l}(298)}\frac{dC_p^{\ l}}{dt}=1.2\times10^{-3}$$

(see Table 5.3) for slope of the $C_p^{\ l}$, $C_p^{\ s}$

◦ 식 (5.1)과 (5.2)에 온도에 따른 Cp 값 계산

(Ex) calculate the heat capacity of polypropylene with a degree of crystallinity of 30% at 25℃ (p.110)

(sol) by the addition of group contributions (see table 5.1)

|  | $C_p^{\ s}$(298K) | $C_p^{\ l}$(298K) |
|---|---|---|
| ( -CH₂- ) | 25.35 | 30.4(from p.111) |
| ( -CH- ) | 15.6 | 20.95 |
| ( -CH₃ ) | 30.9 | 36.9 |
|  | 71.9 | 88.3 |

∴ Cp(298K) = 0.3 (71.9J/mol· K) + 0.7(88.3J/mol· K)
= 83.3 (J/mol· K)

- It is assumed that the semi crystalline polymer consists of an amorphous fraction with heat capacity $C_p^{\ l}$ and a crystalline $C_p^{\ s}$

P 116　Theoretical Background

P 117　The increase of the specific heat capacity with temperature depends on an increase of the <u>vibrational degrees of freedom.</u>

On the basis of the hole theory of liquids, Wunderlich concluded that the difference $C_p^{\ l}$ - $C_p^{\ s}$ at the Tg should be constant per structural bead in the polymer.

A structural bead in this sense is defined as the smallest section of the molecule that can move as unit in internal rotation.

여기서  $\underline{\Delta C_p(T_g)} = C_p^l(T_g) - C_p^s(T_g)$

$C_p^l(T_g)$ : specific heat increment of liquid at $T_g$.
$C_p^s(T_g)$ : specific heat increment of solid at $T_g$.

- 식 (5.1) 과 (5.2)  ,  (p 116) 를 이용하여 $\Delta C_p$ 를 계산할 수 있슴.
- Table 5.5 에 여러 polymer 에 대한 $\Delta C_p$ 값이 계산되어 있슴.

(Table 5.5)   $\Delta C_p$  increase at the $T_g$ .

(ex) polycarbonate(PC) $T_g$ : 151°C
　　　　　　　(계산치)   $\Delta C_p = 56.4/254.3 = 0.222$ (J/g·K)
　　　　　실험에 의한 문헌치        $= 0.222$ (J/g·K)
　　　　　　　　　　　by Kim and Burns, J.A.P.S., <u>34</u> ,945 (1987)

(ex) PET　　　　　$T_g$ : 151°C
　　　　　　　(계산치)   $\Delta C_p = 77.8/192.2 = 0.405$ (J/g·K)
　　　　　실험에 의한 문헌치        $= 0.362$ (J/g·K)
　　　　　　　　　　by Kim and Burns,J.P.S.P, P.Ed.,

Couchman Eq.
$$\ln Tg = \frac{w_1 \Delta Cp_1 \ln Tg_1 + w_2 \Delta Cp_2 \ln Tg_2}{w_1 \Delta Cp_1 + w_2 \Delta Cp_2}$$

P 118　　B. Latent Heat of Crystallization and Fusion (Melting).

$$\Delta H_m(T_m) = H_L(T_m) - H_c(T_m) \text{ , (5.4)}$$

P 119　　$\Delta S_m = \Delta H_m \ / \ T$　　　at melting 에서

♠　<u>Table 5.6 (p.120) 에  각  polymer 에  대한  $\Delta H_m$, $\Delta S_m$, $T_m$ 등을  나타내었다.</u>
　　　　　　　　　　(experimental value or calculated value)

P 124  $H_C(T) = H_C(0) + \int_0^T C_p{}^s dT \qquad (T < T_m) \qquad (5.9)$

$H_L(T) = H_C(0) + \int_0^{T_M} C_P{}^S dT + \int_{T_m}^T C_P{}^L dT + \Delta H_m$

Fig 5.7 에 의해서

$\Delta H_m / C_P{}^L = 0.55 (T_m - T_g) \qquad\qquad\qquad (5.12)$

$\Delta S_m$ 은 식 (5.13) 에 의하여 구할 수 있슴. $\Delta S(0)$ 는 약 2.9 J/mol·K per chain atom.

* At the melting temp, the amorphous and crystalline phase are in equilibrium and the free energy of the melting process is zero.

Example 5.2
   - Estimate the following properties of PET
   a. the specific heat of the solid polymer at 25°C   (298K)
   b. the specific heat of the liquid polymer at spinning temperature (277°C = 550K)
   c. the heat of fusion at the melting point
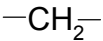   d. the enthalpy difference between the solid and the rubbery form at the $T_g$.

(sol)

   with the data of Tables 5.1 and 5.7
from Table 5.1

| Group | $C_p{}^s(298)$ | $C_p{}^L(298)$ |
|---|---|---|
|  | 4CH$_{ar}$=15.4 x 4=61.7 | 88.8 |
| | 2C$_{ar}$=8.55 x 2=17.1 | 24.4 |
| 2 –CH$_2$- | 2 x 25.35=50.7 | 2 x 30.4=60.8 |

| 2 –COO- | 2 x 46=92 | 2 x 65=130.0 |
|---|---|---|
| | 221.5 | 304.0 |

| Group | $\Delta H_m$ (J / mol ) |
|---|---|
| $-OOC-\langle\bigcirc\rangle-COO-$ | 17,000 |
| $-CH_2-$ | 8,000 |

$$\overline{25,000}$$

From Table 5.7

a. $C_P^S(298) = C_P^S / M = \{221.5(J/mol \cdot K) / 192.2(g/mol)\} * 1000$
$$= 1152(J/Kg \cdot K)$$
   from Table 5.2 , exp. Value = 1130(J/Kg·K)

b. $C_P^L (T) = C_P^L(298)\{0.64 + 0.0012T\}$     (식 5.2)
$$= 304.0 ( 0.64 + 0.66)$$
$$= 395.2$$
   the specific heat will be.
   $C_P^L(550) = 395.2/192.2 \times 1000 = 2056 (J/Kg \cdot K)$
$$\text{Exp. Value} = 2010$$

c. $\Delta H_m = 25000$ , exp. Value = 26900(J/mol)

d. from eq(5.11)

$\Delta H(T_g) = \Delta H(0) = \Delta H_m - \{0.64\ C_P^L(298) - 0.107\ C_P^L(298)\}(T_m - T_g) - \{0.006C_p^L(298) - 0.0015C_p(298)\}(T_m^2 - T_g^2)$

P 124        $H_L(T_g) = H_C(T_g) + \Delta H(0)$

$\underline{\Delta H(T_g)} = H_L(T_g) - H_C(T_g) = \underline{\Delta H(0)}$
                    From Fig.(5.5)     (p. 123)