Chapter 4. Volumetric Properties

A. The volumetric properties are extremely important for nearly every phenomenon or process

(1) Specific volume, molar volumes, densities in the glassy, rubbery, and crystalline state,
(2) Specific and molar thermal expansivities
(3) Specific and molar melt expansion for crystalline polymer.

- 위의 properties 들을 additive group contibution 방법을 이용하여 구할 수 있음

◦ Methods for expressing the additivity within structural units

(1) use of "atomic" contributions
(2) use of "group" contribution
(3) use of "bond" contribution

◦ density = $\dfrac{molar\ mass}{molar\ volume} = \dfrac{M}{V}\dfrac{(g/mol)}{(cm^3/mol)}$ = (g/cm^3)

◦ Van der Waals volume (V_w) – defined as the space occupied by this molecule, and the Van der Waals volume is given by eq(4.1) (p. 73)
(see Table 4.2 for V_w)

◦ V_c (0K) = $V°(0) \approx 1.30V_w$ (4.2)
→ zero point molar volume
→ zero point volume at crystalline state

B. Standard molar volumes at room temp (298K)

(1) Table 4.2 Van der Waals volume을 나타냄
◦ Table 4.2A에는 V° (0) 에 대한 atomic and structural constants

를 나타냄

◦ Table 4.3에는 CH_2에 대한 molar volume을 나타냄

◦ Table 4.4에는 room temp.에서 organic liquid의 molar volume의group contribution을 나타냄

◦ Table 4.5에는 25℃에서 amorphous polymer (무정형 고분자), (rubbery state)에 대한 molar volume을 나타냄.

$$V_r(298K) = \sum_i V_i(298k) \qquad (4.3b)$$

- Table 4.4의 값을 이용하여 rubbery amorphous polymer의molar volume의 값을 Table 4.5에 나타내었다.

  $V_r/V_w = 1.6 \pm 0.035\ (cm^3/mol)$ (p.81 figure 4.1참조)

◦ Molar volume of glassy amorphous polymer

- 이 경우는 T_g (유리전이온도 : glassy transition temperature)가 상온(25℃)보다 높은 고분자인 경우임
  Table 4.6에 glassy amorphous polymer의 molar volume을 나타내었음 $V_g/V_w = 1.6 \pm 0.045(cm^3/mol)$

◦ Molar volume of crystalline polymer at 25℃

- Table 4.7에 fully crystalline polymer의 molar volume을 나타내었다.
  $V_c(298K)/V_w = 1.435 \pm 0.045\ (cm^3/mol)$

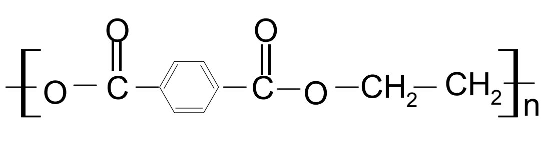
◦ Molar volume of semi crystalline polymers

$$V_{sc} = x_c V_c + (1-x_c)V_a$$

여기서 x_c = degree of crystallinity

Table 4.8에서$\rho_c/\rho \approx 1.13$

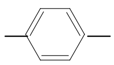
(ex 4.1) Estimate the densities of amorphous & crystalline PET(poly (ethylene terephthalate))



에서

M=192.2(g/mol), 상온에서 amorphous PET는glassy state 이므로 (이유는 PET의T_g가 약 70ºC),

Table 4.9에서

Group	V_g(298K)	V_c(298K)
	65.5 (cm3/mol)	59.0
—COO—	2×23 = 46	221.5 = 43
— CH_2—	2×16.37 = 32.7	2×14.68 = 29.4
	144.2	131.4

$$\rho_g(298K) = \frac{M}{V}\frac{(g/mol)}{(cm^3/mol)} = \frac{192.2}{144.2} = 1.33\ (g/cm^3)$$

실험치는1.33 (g/cm^3)

$$\rho_c(298K) = \frac{192.2}{131.4} = 1.47\ (g/cm^3)$$

실험치는1.48(g/cm^3)

C. Thermal Expansion

1. The Specific thermal expansivity

$$\left(\frac{\partial v}{\partial T}\right)_p \equiv e \qquad (cm^3/g\cdot K)$$

2. The coefficient of thermal expansion

$$\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \equiv \alpha \qquad (K^{-1})$$

3. The linear coefficient of thermal expansion

$$\frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_p \equiv \beta \qquad (K^{-1})$$

4. The molar thermal expansivity

$$\left(\frac{\partial V}{\partial T}\right)_p \equiv E \qquad (\mathrm{cm^3/mol\cdot K})$$

◦ Inferences from the thermal expansion model

1. Numerical values of the molar thermal expansivities

$$E_l = \frac{V_l(T) - V_l(0)}{T} = \frac{V_l(298) - V_c(0)}{298} \approx \frac{V_r(298) - V_c(0)}{298} = E_r \qquad (4.12)$$

$$E_g = \frac{V_g(T) - V_g(0)}{T} \approx \frac{V_c(T) - V_c(0)}{T} = \frac{V_c(298) - V_c(0)}{298} = E_c \qquad (4.13)$$

2. The excess volume of the glassy state

$\Delta V_g = V_g(T) - V_c(T)$: the difference in molar volume of the two solid states of the polymer.

See Table 4.11 (p.92)

$V_r(T) = V_l(T) = V_r(298) + E_l(T-298)$
$V_g(T) = V_g(298) + E_g(T-298) = V_g(298) + E_c(T-298)$
$V_c(T) = V_c(298) + E_c(T-298)$
E_c: molar thermal expansity

(Ex 4.2) Estimate the expasion coefficient of the PET melt and its density at the extrusion temperature of 277℃(550K)

(sol) From eq(4.6)
$e_l = E_l/M \qquad e_g = E_g/M$ 에서
From eq(4.14) and (4.15) molar thermal expansivity는

$E_g = E_c = 0.4510-3V_w$ (Table 4.11)
$= 0.45\times10^{-3}\times94.18 = 4.2\times10^{-2}$
$E_l = 10\times10^{-4}\times94.18 = 9.4\times10^{-2}$

$T_g(PET) = 343K$

$V_l(550) = V_g(298) + E_g(T_g-298) + E_l(550-T_g)$

$= 143.2 + 4.2\times10^{-2}(343-298) + 9.4\times10^{-2}(550-343) = 164.3$

$\therefore \rho_l(550) = M/V_l = 192.2 / 164.4 = 1.17\ (g/cm^3)$

- experimental value = 1.16 g/cm^3(excellent agreement)

* specific thermal expansivity
- $e_l = 9.4\times10^{-2} / 192.2 = 4.9\times10^{-4} (cm^3/g\cdot K)$
  $e_g = 4.2\times10^{-2} / 192.2 = 2.2\times10^{-4} (cm^3/g\cdot K)$
  (excellent agreement with the exp value)

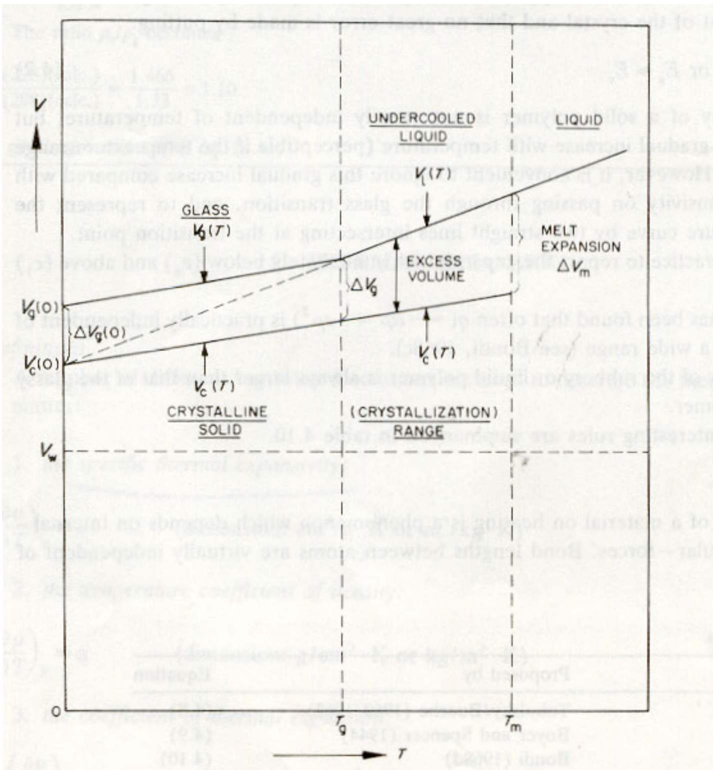


Fig 4.2 Thermal expansion model of polymers (based on a concept of Simha and Boyer)

$$\left.\begin{aligned} V_r(T) &= V_l(T) = V_r(298) + E_l(T-298) \\ V_g(T) &= V_g(298) + E_g(T-298) = V_g(298) + E_c(T-298) \end{aligned}\right\} \quad (4.26)$$

$V_c(T) = V_c(298) + E_c(T-298)$

* Melt density of Polycarbonate at 250℃ ?

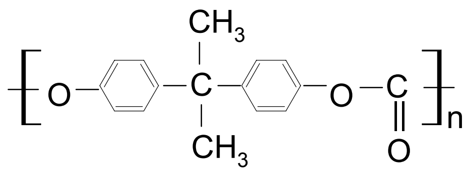
- The formula for molar volume at (273+ 250 = 523K) is

$$V_l(523) = V_g(298) + E_g(T_g-298) + E_l(523-T_g)$$

Where

- V_l is molar volume of the liquid (cm^3/mol)
- V_g is the molar volume of glassy polymer at 25℃ (see Table 4.5)
- E_g is the molar thermal expansivity ($cm^3/g{\cdot}K$) in the glassy state
- E_l is the molar thermal expansivity in the liquid state ($cm^3/g{\cdot}K$)

Polycarbonate의 구조 :



여기서 $V_g(298) = M_{pc} / \rho_{pc} = 254.3/1.20 = 211.92(cm^3/mol)$

polycarbonate의

$E_g = 613\times10^{-4}$ ($cm^3/mol.K$) (see p.94)

$E_l = 1362\times10^{-4}$ ($cm^3/mol.K$) (see p.94)

$T_g = 148 + 273 = 421K$

$$\therefore\ V_l(523) = V_g(298) + E_g(T_g-298) + E_l(523-T_g)$$
$$= 211.92(cm^3/mol) + 613\times10^{-4}(421-298)$$
$$+ 1362\times10^{-4}(523-421)\ (cm^3/mol)$$
$$= 233.35\ (cm^3/mol)$$
$$\therefore\ \rho(523K) = M_{pc}/V_l(523) = 1.089(g/cm^3)$$
$$M_{pc}=254.3(g/mol)$$

◦ Melt densities of literature and calculated value*

* Kim and Burns, Polym.Eng.Sci., 28, 1115(1988)

Polymers	Densities[a]	Melt Densities (g/cm3)[b]

		Literature	Calculated[c]
PC	1.200	1.080[d]	1.089
PS	1.050	0.950[e]	0.941
SAN	1.078	-	0.973
PBT	1.389	-	1.200

a Densities at 25℃ (g/cm3)

b Densities at 25℃

c Estimated from Van Drevelen (1980)

d Z. Dobkowski, Polimery(Warsaw), 25, 110 (1978)

e Chee and Rudin (1973)

(Ex) 170℃에서 polypropylene의 melt density?

(hint) PP의 T_g는 약 -10℃(263K)

(sol) $V_l(273+170) = V_r(298) + E_l(443-298)$

$= 49.5(cm^3/mol) + 314\times10^{-4}(443-298)$

$= 54.05\ (cm^3/mol)$

$\therefore\ \rho\ (443K) = M/V_l = 42.1 / 54.05 = 0.779\ (g/cm^3)$