

## 7.1: Volume Properties

Two volume properties of a closed system are defined as follows:

$$\text{cubic expansion coefficient } \alpha \stackrel{\text{def}}{=} \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \quad (7.1.1)$$

$$\text{isothermal compressibility } \kappa_T \stackrel{\text{def}}{=} -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \quad (7.1.2)$$

The cubic expansion coefficient is also called the coefficient of thermal expansion and the expansivity coefficient. Other symbols for the isothermal compressibility are  $\beta$  and  $\gamma_T$ .

These definitions show that  $\alpha$  is the fractional volume increase per unit temperature increase at constant pressure, and  $\kappa_T$  is the fractional volume decrease per unit pressure increase at constant temperature. Both quantities are *intensive* properties. Most substances have positive values of  $\alpha$ , and all substances have positive values of  $\kappa_T$ , because a pressure increase at constant temperature requires a volume decrease.

The cubic expansion coefficient is not always positive.  $\alpha$  is negative for liquid water below its temperature of maximum density, 3.98 °C. The crystalline ceramics zirconium tungstate ( $\text{ZrW}_2\text{O}_8$ ) and hafnium tungstate ( $\text{HfW}_2\text{O}_8$ ) have the remarkable behavior of contracting uniformly and continuously in all three dimensions when they are heated from 0.3 K to about 1050 K;  $\alpha$  is negative throughout this very wide temperature range (T. A. Mary et al, *Science*, **272**, 90–92, 1996). The intermetallic compound YbGaGe has been found to have a value of  $\alpha$  that is practically zero in the range 100–300 K (James R. Salvador et al, *Nature*, **425**, 702–705, 2003).

If an amount  $n$  of a substance is in a single phase, we can divide the numerator and denominator of the right sides of Eqs. 7.1.1 and 7.1.2 by  $n$  to obtain the alternative expressions

$$\alpha = \frac{1}{V_m} \left( \frac{\partial V_m}{\partial T} \right)_p \quad (7.1.3)$$

(pure substance,  $P=1$ )

$$\kappa_T = -\frac{1}{V_m} \left( \frac{\partial V_m}{\partial p} \right)_T \quad (7.1.4)$$

(pure substance,  $P=1$ )

where  $V_m$  is the molar volume.  $P$  in the conditions of validity is the number of phases. Note that only intensive properties appear in Eqs. 7.1.3 and 7.1.4; the amount of the substance is irrelevant. Figures 7.1 and 7.2 show the temperature variation of  $\alpha$  and  $\kappa_T$  for several substances.

If we choose  $T$  and  $p$  as the independent variables of the closed system, the total differential of  $V$  is given by

$$dV = \left( \frac{\partial V}{\partial T} \right)_p dT + \left( \frac{\partial V}{\partial p} \right)_T dp \quad (7.1.5)$$

With the substitutions  $(\partial V/\partial T)_p = \alpha V$  (from Eq. 7.1.1) and  $(\partial V/\partial p)_T = -\kappa_T V$  (from Eq. 7.1.2), the expression for the total differential of  $V$  becomes

$$dV = \alpha V dT - \kappa_T V dp \quad (7.1.6)$$

(closed system,  
 $C=1, P=1$ )

To find how  $p$  varies with  $T$  in a closed system kept at constant volume, we set  $dV$  equal to zero in Eq. 7.1.6:  $0 = \alpha V dT - \kappa_T V dp$ , or  $dp/dT = \alpha/\kappa_T$ . Since  $dp/dT$  under the condition of constant volume is the partial derivative  $(\partial p/\partial T)_V$ , we have the general relation

$$\left( \frac{\partial p}{\partial T} \right)_V = \frac{\alpha}{\kappa_T} \quad (7.1.7)$$

(closed system,  
 $C=1, P=1$ )

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