

7.1: Volume Properties

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

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

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

The cubic expansion coefficient is also called the coefficient of thermal expansion and the expansivity coefficient.

Other symbols for the isothermal compressibility are β and γ_T .

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

The cubic expansion coefficient is not always positive. α is negative for liquid water below its temperature of maximum density, 3.98 °C. The crystalline ceramics zirconium tungstate (ZrW_2O_8) and hafnium tungstate (HfW_2O_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; α 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 α 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 α and κ_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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