Section A. Nomenclature Topics

Part II. Thermal Coefficients, Energy, and Work

Chapter 5. Thermal Coefficients

LECTURE 6. INTERRELATION BETWEEN THERMAL COEFFICIENTS

§ 1.7. Thermal coefficients and connection between them

Thermal coefficients characterize **heating and elastic (resilient) properties of bodies** [113, pp. 20-22]. There are known the **coefficient of volumetric expansion** α, the **thermal coefficient of pressure** β, and **isothermal coefficient of compressibility** γ.

At heating up some certain mass of a substance at a constant external pressure, the change of the volume per each degree of the temperature rise is expressed through the partial derivative [113, p. 20]

$$\left(\frac{dV}{dT}\right)_p.$$

The relative change of the volume at heating up in one degree is called the **coefficient of volumetric expansion** [113, p. 20, (2.11)]

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p. \tag{2.11}$$

For an ideal gas $\alpha = \frac{1}{T}$.

If the temperature is expressed in degrees by Celsius, then

$$dt = dT$$

and relative change of volume can be represented with the ratio of the derivative of

$$\frac{dV}{dt}$$

to the volume of V_0 at 0 °C, i.e. (that is)

$$\alpha_0 = \frac{1}{V_0}\left(\frac{\partial V}{\partial t}\right)_p .$$

If one can assume $\alpha = \text{const}$ in a short (narrow) interval of the temperature change, then

$$\alpha_0 V_0 = \left(\frac{\partial V}{\partial t}\right)_p = \text{const} .$$

Integrating, we come to the conclusion

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$$V = V_0(1 + \alpha_0 t).$$

For the ideal gas at any pressure

$$\alpha_0 = \frac{1}{273.15} = 0.00366 \ \frac{1}{{}^{\circ}C} .$$

If one is heating a given mass of a substance at a constant volume, then the relative change of the pressure at the change of the temperature is characterized with the **thermal coefficient of pressure** β [113, p. 20, (2.12)]

$$\beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_v , \qquad (2.12)$$

where p – the pressure at the temperature T.

For an ideal gas $\beta = \alpha = \frac{1}{T}$.

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$$\beta_0 = \frac{1}{p_0}\left(\frac{\partial p}{\partial t}\right)_v .$$

At a small change of the temperature, one can evaluate (recon, judge) $\beta = \text{const}$

$$\beta_0 p_0 = \left(\frac{\partial p}{\partial t}\right)_v = \text{const} .$$

$$p = p_0(1 + \beta_0 t).$$

For an ideal gas $\beta_0 = \alpha_0$.

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At the isothermal compression of a given mass of a substance, the ration of the change of the volume at the change of the pressure in one unit of the pressure to the volume is called the **isothermal coefficient of compressibility** [113, p. 21, (2.13)]

$$\gamma = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T . \qquad (2.13)$$

The sign minus means a decrease of volume with an increase of pressure.

For ideal gases by the Boyle's-Mariotte's law [113, p. 21, (see § 4.4)]

$$V = \frac{\text{const}}{p} .$$

Differentiating with respect to pressure, we get

$$\left(\frac{\partial V}{\partial p}\right)_T = -\frac{\text{const}}{p^2} = -\frac{1}{p}V .$$

$$\gamma = \frac{1}{p} .$$

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The interrelation between the thermal coefficients of α, β, and γ in the general case [113, p. 21, (for more details see § 2.10)]

$$dp = \left(\frac{\partial p}{\partial T}\right)_V dT + \left(\frac{\partial p}{\partial V}\right)_T dV\,; \qquad \text{(a)}$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp\,; \qquad \text{(b)}$$

$$dT = \left(\frac{\partial T}{\partial p}\right)_V dp + \left(\frac{\partial T}{\partial V}\right)_p dV\,. \qquad \text{(c)}$$

Substituting dp from the first equation of (a) into the second equation of (b)

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T \left[\left(\frac{\partial p}{\partial T}\right)_v dT + \left(\frac{\partial p}{\partial V}\right)_T dV\right] =$$

$$= \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v dT + \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T dV\,,$$

taking into consideration that

$$\left(\frac{\partial V}{\partial p}\right)_T = \left(\frac{\partial p}{\partial V}\right)_T^{-1},$$

we will get

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v dT + dV\,,$$

$$0 = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v dT + dV - dV =$$

$$= \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v dT\,,$$

$$dT\left[\left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v\right] = 0\,,$$

$$\left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v = 0\,,$$

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v\,,$$

[113, p. 22, (2.14)]

$$\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v} = -1. \qquad (2.14)$$

From (2.11), (2.12), (2.13)

$$\alpha V = \left(\frac{\partial V}{\partial T}\right)_p , \qquad (2.11a)$$

$$\beta p = \left(\frac{\partial p}{\partial T}\right)_v , \qquad (2.12a)$$

$$-\gamma V = \left(\frac{\partial V}{\partial p}\right)_T . \qquad (2.13a)$$

Substituting (2.11a), (2.12a), (2.13a) into (2.14) [113, p. 22, (2.15)]

$$\frac{\alpha V}{-\gamma V \cdot \beta p} = -1, \qquad \frac{\alpha}{\gamma \cdot \beta p} = 1, \qquad \alpha = \beta \cdot \gamma \cdot p . \qquad (2.15)$$

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