

PART - I

INTRODUCTION

1. Thermal Expansion and the Equation of State of Solids.

It should be possible to sum up the macroscopic response of solids to various physical stimuli in an equation of state of solids. An equation of state of solids, however, can not be a simple statement of the relationship between pressure, volume and temperature of the solids. It is bound to be much more complicated. The stress in a solid can be more complicated than a pressure and a strain more complicated than a mere change in volume. The solid, for instance, can undergo shear. However, the partial success of Vander Wall's equation in explaining the behaviour of liquids encouraged attempts to extend that equation with some modifications to the solid state of matter. Innumerable attempts have been made in this direction since the middle of the last century. A detailed account of the proposed equations has been given by Partington¹. These equations, however, are mostly of historical importance. Nevertheless, an equation proposed in the first decade of this century by Gruneisen² has attracted much attention.

Gruneisen's theory was originally empirical in nature but was later deduced on the basis of the lattice potential envisaged by Mie³. Gruneisen's theory leads to a $(V-T)$ relation in terms of compressibility and several other variables. Several forms of Gruneisen's equation are available. HumeRothery⁴ has made a thorough survey of the various forms of Gruneisen's equation and has concluded that the form due to Simon and Vohsen⁵ is most representative of experimental data. The Gruneisen's

equation in this form is given by the relationship

$$\frac{V_T - V_0}{V_0} = \frac{E_T}{Q_0 - k E_T} \quad \dots (1)$$

where

V_T, V_0 = volumes of a solid at $T^\circ\text{K}$ and 0°K respectively.

$$E_T = \int_0^T C_v dT, \quad C_v \text{ being the atomic heat at constant volume.}$$

$$Q_0 = \frac{V_0}{K_0 \gamma}$$

K_0 = compressibility at 0°K .

$$\gamma = - \frac{d \log \nu}{d \log V} \quad = \text{a constant, known as Gruneisen's constant.}$$

ν = frequency of lattice vibrations.

$$k = \frac{m + n + 3}{6}, \quad \text{a constant.}$$

m, n = exponents in the Mie equation for energy

$$\phi = a/r^m + b/r^n$$

a and b being constants and r the interparticle distance.

Debye⁶, Born and Bradburn⁷, Bradburn⁸, Fürth⁹, Corson¹⁰ and few other workers have also proposed several equations of state of solids laying emphasis on different properties of solids.

The equation of state of solids being basically a relation between p, V and T in terms of other variables, the

thermal expansion or (V,T) relationship is a partial expression of it. Thus, the study of thermal expansion of solids is of great importance in arriving at a proper equation of state of solids.

2. Mechanism of Thermal Expansion of Solids.

Thermal expansion has been attributed to the anharmonicity of atomic oscillations. With the change in temperature there is a shift of the mean position of the oscillating atom due to the asymmetric potential energy diagram. The macroscopic effect of this change in the mean position of the atom is the thermal expansion or contraction. Let us consider the effect of anharmonic terms in the potential energy on the separation of a pair of atoms at a temperature T. Taking the potential energy of the atoms at a displacement x from their equilibrium position at 0°K as

$$V(x) = px^2 - qx^3 - rx^4 \dots \quad \dots (2)$$

we have the average displacement

$$\bar{x} = \frac{\int_{-\infty}^{\infty} x e^{-V(x)/kT} dx}{\int_{-\infty}^{\infty} e^{-V(x)/kT} dx} \quad \dots (3)$$

by using Maxwell-Boltzmann distribution function. For small displacements corresponding to low anharmonic energy,

$$\bar{x} = \frac{3 k.T.q}{4 p^2} \quad \dots (4)$$

giving a constant value of the temperature coefficient of thermal expansion

Since kT is the classical mean energy \bar{E} of the oscillator in the harmonic approximation, we may write

$$\bar{x} = 3E_0 / 4p^2 \quad \dots (5)$$

The corresponding quantum mechanical result will be obtained by substituting for E the energy of a harmonic oscillator in quantum mechanics. In this case, the thermal expansion is expected to decrease abruptly as the temperature drops below the characteristic temperature of the oscillator and to vanish at absolute zero. This is the observed behaviour of solids. Moreover, the third law of thermodynamics also requires that the thermal expansion should tend to become zero at absolute zero.

Megaw¹¹ has attempted to explain qualitatively the thermal expansion of nonmetallic crystals in terms of their structure and interatomic forces. She has based her calculations on the Debye relationship for cubic monatomic crystals, and has obtained

$$\alpha = \frac{1}{2} \cdot \frac{(n+2)}{n} \cdot \frac{C_v}{\phi} \quad \dots (6)$$

where α = coefficient for thermal expansion

C_v = specific heat at constant volume.

ϕ = lattice energy of the cubic substance.

n = the power of the repulsive term in the Mie expression.

For a polar crystal,

$$\phi = \phi_{(\alpha)} (1 + 1/n) \quad \dots (7)$$