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STUDY OF THERMODYNAMIC IDENTITIES FOR SOLIDS

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Abstract

We have obtained and discussed a number of identities for thermal expansivity, bulk modulus, Grüneisen parameter, specific heat and other related properties. We have demonstrated the usefulness of thermodynamic and thermoelastic properties of solids at high pressures and high temperatures.

Keywords: Thermodynamic identities, thermodynamic function, thermal expansivity, specific heat, Grüneisen parameters.

INTRODUCTION

Anderson [1] listed the thermodynamic identities used in his book, many of which are well Known [2-5]. Relationships of classical thermodynamics are very helpful in determining physical properties at extreme conditions because many of the needed experimental data cannot be obtained. The chief experimental information on the interior of the earth is taken from seismic data, so the thermodynamic relationships appropriate to geophysical problems are often recast emphasizing elastic properties. Compensating for the limited kinds of measurements available in high P, high T materials science is a set of relationships and approximations, set forth below, not customarily emphasized in thermodynamics as found in physics and chemistry text books. With these identities a temperature measurement, done isobarically can be converted to pressure information .Conversely, an isothermal pressure measurement can be converted to temperature information. As we shall see, some thermodynamic identities can easily be transformed into differential equations to help construct a theory aimed at showing how a physical property can be defined at extreme P and T.

Useful relationships are easily derived from Maxwell's relations [6]

$$-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S \quad (1)$$

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S \quad (2)$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad (3)$$

$$-\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T \quad (4)$$

Rewriting Maxwell's relations so as to incorporate the Grüneisen ratio $\gamma$and other measurable parameters, we have

$$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V = \frac{-\gamma T}{V} \quad (5)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P = \frac{\gamma T}{B_S} \quad (6)$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T = \alpha V \quad (7)$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T = \alpha B_T \quad (8)$$

It is well known that the computations of thermodynamic functions (entropy, for example) require knowledge of the thermal expansivity α and compressibility κ as well as the specific heat. The pressure (or volume) and the temperature variation of α and κ contribute to the pressure (or volume) and the temperature variation of the thermodynamic functions . The tabulation of these thermodynamic functions in the extreme ranges of temperature and pressure requires a good understanding of the EOS, elasticity at very high temperature, anharmonicity of the solid and thermal expansivity at high temperature.Recent experimental progress in the thermal EOS has clarified the volume and high temperature corrections to the thermal pressure P_{TH} and to the isothermal bulk modulus B_T (the reciprocal of compressibilityκ) for MgO, Mg_2SiO_4 and Al_2O_3 [7-9]. This progress is represented by the ability to measure elastic constants at high temperatures (in fact, as high as 1825K) using new resonance measurement techniques [10].

The product αB_T is an important correction needed for evaluating entropy at high compression and volume .It has become apparent in the last 10 years that it is best to treat αB_T as a single parameter as the product varies little with pressure or temperature, whereas both α and B_T each varies significantly with pressure and with temperature. Birch [11] first proposed that for silicates and oxides, to a good approximation,αB_T should be independent of pressure. He based this idea on experiment made by Bridgman [11] on alkali metals upto 3 GPa. Anderson [12] proposed that at high temperatures αB_T is independent of T for oxides and silicates, and he followed up with a review paper that confirmed this for many oxides and silicates [13].Some basic identities are given below:

$$\frac{1}{T}\left(\frac{\partial C_V}{\partial V}\right)_T \equiv \left[\frac{\partial(\alpha B_T)}{\partial T}\right]_V \quad (9)$$

$$\left(\frac{\partial B_T}{\partial T}\right)_V \equiv -V\left[\frac{\partial(\alpha B_T)}{\partial V}\right]_T \quad (10)$$

$$B_T \equiv \left(\frac{\partial P}{\partial T}\right)_V \quad (11)$$

$$B_T^{2}\left(\frac{\partial\alpha}{\partial P}\right)_T \equiv \left(\frac{\partial B_T}{\partial T}\right)_P \qquad (12)$$

$$B_T\left(\frac{\partial\alpha}{\partial T}\right)_V = \left(\frac{\partial(\alpha B_T)}{\partial T}\right)_P \qquad (13)$$

Value of α, the volume thermal expansivity defined as $(1/V)(\partial V/\partial T)_P$ enters into so many properties and thermoelastic parameters that it must be especially emphasized. In several thermoelastic parameters, α is a factor in the equation; eg $\gamma = (\partial B_T V/C_V)$;$\delta_T = -(1/\alpha B_T)(\partial B_T/\partial T)_P$. Thus errors in the value of α strongly affect computation of thermodynamic quantities. A horough understanding of α is necessary in dealing with several problems arising in equations of state. The importance of knowing the value of the thermal expansivity of candidate materials of the earth's mantle at P, T conditions of the lower mantle is well recognized. Attempts to find the high T, high P values of α for mantle minerals have been made by Anderson [14], Kinttle et al [15], Mao et al [16] ,Chopelas and Boehler [17], Hemley et al [18], Anderson et al [19] and Wang et al [20]. The main thermodynamic expression giving the relationship between α and V is a thermodynamic identity, as discussed by Anderson [14] and Birch [21] but strongly emphasized by D. L. Anderson[20].

$$\delta_T \equiv \left(\frac{\partial \ln \alpha}{\partial \ln V}\right)_T \qquad (14)$$

An important dimensionless parameter is the ratio of $(\partial B_T/\partial T)_P$ to αB_T , $-\delta_T$. It is a thermoelastic parameter related to the variation of α with density often called the Anderson-Grüneisen parameter [23] but earlier called the second Grüneisen parameter [24].

$$\delta_T = \left(\frac{\partial \ln B_T}{\partial \ln V}\right)_P = \frac{-1}{\alpha B_T}\left(\frac{\partial B_T}{\partial T}\right)_P \qquad (15)$$

The identity (4.14) is derived by combining (15) with the better known identity $B_T^2(\partial\alpha/\partial P)_T \equiv (\partial B_T/\partial T)_P$[14, 21]. A related dimensionless parameter arising from the ratio of $(\partial\alpha/\partial T)_P$ to α^2 is

$$\hat{\alpha} = \frac{1}{\alpha^2}\left(\frac{\partial\alpha}{\partial T}\right)_P \qquad (16)$$

η is dimensionless variable often called the dilation, $\eta = V/V_0$ which shall be called compression where the subscript 0 indicates V at zero pressure. Some identities are given below:

$$\frac{\partial^2 B_T}{\partial P\,\partial T} = \delta_T\left(\frac{\eta}{B_T}\right)\left[\frac{\partial(\alpha B_T)}{\partial\eta}\right]_T + \alpha\mu\left(\frac{\partial\delta_T}{\partial\eta}\right)_T$$

$$\equiv \alpha\delta_T(\delta_T - B' + \kappa) \qquad (17)$$

$$\kappa = \left(\frac{\partial \ln \delta_T}{\partial \ln \eta}\right)_T \qquad (18)$$

$$\left(\frac{\partial \ln(\alpha B_T)}{\partial \ln V}\right)_T \equiv \delta_T - B' \quad (19)$$

$$\left[\frac{\partial \ln(\alpha B_T)}{\partial P}\right]_T \equiv \frac{B' - \delta_T}{B_T} \quad (20)$$

$$\left[\frac{\partial(\alpha B_T)}{\partial T}\right]_P \equiv \alpha^2 B_T(\hat{\alpha} - \delta_T) \quad (21)$$

where $\hat{\alpha}$ is given by Eq. (16)

$$\left(\frac{\partial C_V}{\partial V}\right)_T \equiv \alpha(\alpha B_T)T(\hat{\alpha} + B' - 2\delta_T) \quad (22)$$

$$\left(\frac{\partial C_V}{\partial P}\right)_T \equiv -\alpha^2 TV(\hat{\alpha} + B' - 2\delta_T) \quad (23)$$

$$\left(\frac{\partial B_T}{\partial T}\right)_V \equiv \alpha B_T(B'_T - \delta_T) \quad (24)$$

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