

## Equation of state for inert gas solids

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**Abstract.** The equation of state is a fundamental relation to analyse the thermophysical properties of different class of solids and it plays a key role in basic and applied condensed matter physics research. A lot of work has been done in the field of ionic solids, minerals and metals but a very little work is done in the field of inert gas solids. Most of the equations of state failed to explain the properties of inert gas solid because of their abnormal behavior in the low temperature range. In the present paper, Singh–Gupta equation of state has been used to study the properties of these solids. The results obtained using these equations have shown a good agreement with available experimental results. Thus it is shown that these equations of states successfully explain the behavior of inert gas solids.

**Keywords.** Equation of state; inert gas solids; thermal expansion; bulk modulus.

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### 1. Introduction

Much of the physical world around us and a large part of modern technology are based on solid materials. So it is interesting to study the behavior and thermophysical properties of different solids. In the present work, equations of state (EOS) are applied to study the thermophysical properties of inert gas solids. The inert gas solids (IGS) or rare gas solids (RGS), neon, argon, krypton and xenon, have been used as model substances for lattice dynamic calculations of thermodynamic properties. These crystals are transparent, insulators and weakly bonded with very low melting points. Since the IGSs have closed electronic shells unlike other solids, their thermodynamic properties such as bonding, thermal expansion, compression, bulk modulus, thermal expansion coefficient and heat capacity are entirely different from other classes of solids (metals, semiconductors etc.). These crystals have fcc structure. The combination of long-range van der Waals attractive interaction (induced by dipole–dipole interaction) and short-range repulsive interaction (arises due to overlapping of charge distribution) gives the total energy of two atoms and the potential is the well-known Lennard–Jones potential [1]. Most of the theoretical

calculations of IGS are based on the Lennard–Jones potential model. But in the present study a thermodynamic approach is used to calculate thermal expansion, bulk modulus and thermal expansion coefficient of these solids. The major objective of theoretical calculation on inert gas solids is to test the applicability of equation of state, when the temperature range is from a very low reference temperature to their melting points.

The EOS is basically a pressure–volume–temperature relationship. The studies based on EOS are widely important not only in physics but also in chemistry and geophysics [2–6]. The theoretical studies of EOS at different pressures and temperatures are of fundamental interest as they permit interpolation and extrapolation to the region in which the experimental data are not available. The present work describes the theoretical study of thermophysical properties especially compression, thermal expansion, bulk modulus, and thermal expansion coefficient of inert gas solids. The relation between pressure ( $P$ ) and volume ( $V$ ) at a constant temperature ( $T$ ) is known as isothermal EOS while the relation between volume ( $V$ ) and temperature ( $T$ ) at fixed pressure is known as isobaric EOS. The present study is based on Singh–Gupta isobaric equation of state. These equations were basically developed to study high-temperature behavior of minerals and metals for geological applications but in the present study, these equations are used for inert gas solids at very low-temperature range. Most of the equations of state such as Vinet *et al*, [7], Shanker *et al* [8], Suzuki [9], Poirier and Tarantola [10] and Hama and Suito [11] do not explain the thermophysical properties of solids in all ranges of temperatures but it is found that the equations obtained by Singh and Gupta [3] are valid in low-temperature range also. A lot of work has been done for the minerals [12,13], metals and semiconductors [14,15] but the inert gas solids are still untouched.

## 2. Method of analysis

Thermal expansion in solids is due to the large amplitudes of lattice vibrations at high temperature and hence inter-atomic separation also increases on increasing the temperature of the solid. The equation of state for the analysis of thermal expansion coefficient can also be derived in terms of only the variable parameter temperature. Recent theoretical studies suggest that  $\alpha B_T$  is insensitivity to volume over a range of temperatures. In the case of inert gas solids the range of temperature is very small because these solids exist in a small range of temperature and there should not be any variation in the value of  $\alpha B_T$ . Regardless of the exact value of  $\alpha B_T$  it can be assumed that under the effect of temperature the product of thermal expansion coefficient and bulk modulus remains constant [1,6] and can be given as

$$\alpha B_T = \text{constant}, \quad (1)$$

where  $\alpha$  is the volume thermal expansion coefficient and  $B_T$  is the bulk modulus. On differentiating eq. (1) with respect to  $T$ , at constant pressure we get

$$\left( \frac{dB_T}{dT} \right)_P = -\frac{B_T}{\alpha} \left( \frac{d\alpha}{dT} \right)_P. \quad (2)$$

The Anderson–Gruneisen parameter  $\delta_T$  [6,16] is defined as

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$$\delta_T = -\frac{1}{\alpha B_T} \left( \frac{dB_T}{dT} \right)_P. \quad (3)$$

Substituting eq. (2) in eq. (3) we get

$$\delta_T = \frac{V}{\alpha} \left( \frac{d\alpha}{dV} \right)_P. \quad (4)$$

Gruneisen parameter is basically a measurement of anharmonicity in a crystal. Recent studies revealed that  $\delta_T$  changes with temperature and it must be considered as a temperature-dependent parameter [12]. In the present work the empirical relation for temperature dependence of  $\delta_T$  is given as follows:

$$\delta_T = \delta_T^0 \left( \frac{T}{T_0} \right)^k, \quad (5)$$

where  $T_0$  is the reference temperature and  $\delta_T^0$  is the value of Anderson–Gruneisen parameter ( $\delta_T$ ) at  $T = T_0$  and  $k$  is new dimensionless thermoelastic parameter, whose value is calculated by the slope of the graph plotted between  $\log(\delta_T)$  and  $\log(T/T_0)$ . Using eqs (3) and eq. (5) and solving we get

$$\alpha_T = \alpha_0 \left[ 1 - \frac{\delta_T^0 \alpha_0}{T_0^k (k+1)} \{T^{k+1} - T_0^{k+1}\} \right]^{-1}. \quad (6)$$

where  $\alpha_0$  is the thermal expansion coefficient at reference temperature  $T_0$ . This equation requires only three input parameters  $\alpha_0$ ,  $\delta_T^0$  and  $k$  at room temperature and the value of  $\alpha_T$  is evaluated directly as a function of temperature.

Using eqs (3) and (5) and integrating we get the expression for bulk modulus  $B_T$  as

$$B_T = B_0 \left[ 1 - \frac{\alpha_0 \delta_T^0}{T_0^k (k+1)} \{T^{k+1} - T_0^{k+1}\} \right], \quad (7)$$

where  $B_0$  is the bulk modulus at reference temperature  $T_0$ . Thus the value of bulk modulus  $B_T$  as a function of temperature can be calculated from eq. (7). Similarly, using eq. (3) the expression for the volume thermal expansion ( $V/V_0$ ) can be obtained as

$$\frac{V}{V_0} = \exp \left[ \int_{T_0}^T \frac{\alpha_0}{\left[ 1 - \frac{\alpha_0 \delta_T^0}{T_0^k (k+1)} \{T^{k+1} - T_0^{k+1}\} \right]} dT \right]. \quad (8)$$

The value of volume thermal expansion as a function of temperature for different inert gas solids have been calculated by eq. (8) which is known as Singh–Gupta’s integral form of equation of state.

**Table 1.** Input parameters with their corresponding references. The square brackets show the reference sources.

Solids	Structure	Reference temp. (K)	$B_0$ (GPa)	$B'_0$	$\alpha_0$ ( $10^{-5} \text{ K}^{-1}$ )
Ar	fcc	40	2.18 [17]	7.5 [17]	106.8 [17]
Kr	fcc	60	2.55 [17]	7.3 [17]	90.5 [17]
Xe	fcc	60	3.67 [18]	4.48 [19]	60.0 [20]

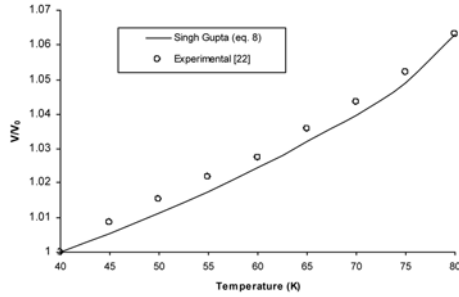
**Table 2.** Thermal expansion, bulk modulus and thermal expansion coefficient of Ar.

$T$ (K)	$V/V_0$		$B_T$ (GPa)		$\alpha$ ( $10^{-5} \text{ K}^{-1}$ )	
	Singh-Gupta (eq. (8))	Experimental [22]	Singh-Gupta (eq. (7))	Experimental [17]	Singh-Gupta (eq. (6))	Experimental [17]
40	1	1	2.18	2.18	106.8	106.8
45	1.0054	1.0087	2.07		111.42	
50	1.0112	1.0173	1.96	1.98	116.83	125.4
55	1.0174	1.0217	1.85		123.19	
60	1.0244	1.0304	1.72	1.75	130.69	145.0
65	1.0313	1.0369	1.59		139.64	
70	1.0391	1.0434	1.46	1.51	150.42	169.9
75	1.0479	1.0521	1.32		163.61	
80	1.0470	1.0630	1.17	1.20	180.04	203.1

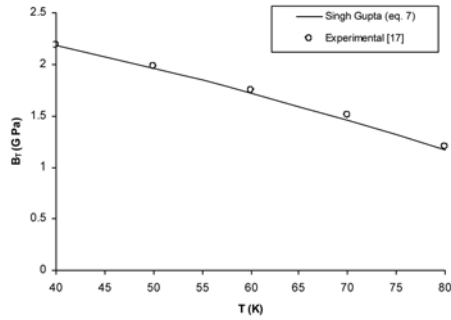
**Table 3.** Thermal expansion, bulk modulus and thermal expansion of Kr.

$T$ (K)	$V/V_0$		$B_T$ (GPa)		$\alpha$ ( $10^{-5} \text{ K}^{-1}$ )	
	Singh-Gupta (eq. (8))	Singh-Gupta (eq. (7))	Experimental [17]	Singh-Gupta (eq. (6))	Experimental [17]	
60	1	2.55	2.55	90.50	90.5	
65	1.0046	2.46		93.56		
70	1.0094	2.37	2.30	97.12	98.7	
75	1.0144	2.27		101.13		
80	1.0197	2.18	2.05	105.68	107.3	
85	1.0252	2.07		110.86		
90	1.0310	1.97	1.90	116.79	117.6	
95	1.0372	1.86		123.62		
100	1.0439	1.75		131.56		
105	1.0510	1.63		140.80		
110	1.0587	1.51		151.99		
115	1.0675	1.39		165.36		
120	1.0764	1.26		181.78		

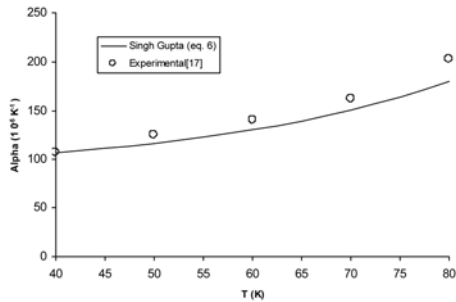
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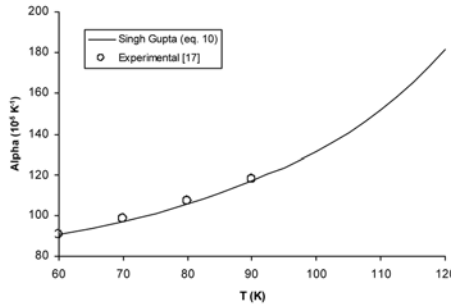
**Figure 1.** Thermal expansion of solid Ar from reference temperature to melting temperature.



**Figure 2.** Variation in bulk modulus of Ar with temperature.



**Figure 3.** Variation in thermal expansion coefficient of Ar with temperature.



**Figure 6.** Variation in thermal expansion coefficient with temperature of Kr.

### 3. Results and discussion

In our present research work, we have analysed the thermophysical properties, i.e. thermal expansion and bulk modulus, using eqs (8) and (9) with their explanations. Equations (6)–(8) are isobaric EOS and are used to calculate the thermal expansion coefficient, bulk modulus and thermal expansion of inert gas solids. The applications of these equations of state are thus fully tested by calculating their thermophysical properties. The input parameters such as bulk modulus ( $B_0$ ), first pressure derivative of bulk modulus ( $B'_0$ ) and the volume thermal expansion ( $\alpha_0$ ) at zero pressure and reference temperature are given in table 1 with their corresponding references. The values of dimensionless parameter  $k$  can be calculated from the graph between  $\log \delta_T$  and  $\log(T/T_0)$  as represented by eq. (8) [6]. The value of  $k$  may also be obtained by curve fitting method. In the case of inert gas solids the value of  $k$  is estimated to be 0.6 [21]. The temperature range is from a reference temperature to their melting points. Neon is excluded from the present study because its melting point is very low (24 K) and neon solid cannot be studied in such a limited range of temperatures.

The values of thermal expansion ( $V/V_0$ ), bulk modulus ( $B_T$ ) and thermal expansion coefficient ( $\alpha_T$ ) of inert gas solids, Ar, Kr, and Xe, have been calculated by eq. (8), eq. (7), and eq. (6) respectively. The results obtained are listed in tables 2, 3 and 4 with the corresponding experimental data. The results are also represented in graphs (figures 1–6) for the sake of comparison. It is observed from the tables and graphs that the values of thermal expansion, bulk modulus and thermal expansion coefficients of these solids calculated by these equations are very close to the available experimental data, and results show the validity of these equations. The experimental data for Xe are not available till now but the calculated values have been predicted, which will be useful for further research in this field. These equations of states can also be employed to study the thermophysical properties of other classes of solids such as semiconductors and metals. On the basis of overall descriptions, it may thus be concluded that Singh–Gupta equation of state successfully analyse the thermophysical properties of not only minerals but also inert gas solids (for table 4 and figures 4 and 5, please see <http://www.ias.ac.in/pramana/v69/p312a>).

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