

Analysis of Temperature Dependence of Volume Expansion for Geophysical Minerals

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Abstract: In present communication, we have developed a method for estimating temperature dependence of volume thermal expansion of geophysical minerals at high pressures by modifying the formulation originally due to Anderson (1995); Stacey and Davis (2004). The values used in present work are those reported by Anderson in the form of density data. The method has been applied to the temperature dependence of thermal pressure for Mg_2SiO_4 , $MgAl_2O_4$, MnO , Fe_2SiO_4 , $NaCl$ and KCl were carried out in our study. Computed values are compared with available experimental values. The model is extended to study the compression behavior at different temperature. A good agreement obtained between theory and experiment demonstrates the validity of the present approach.

Keywords: Volume expansion, Thermal pressure, Equation of state, Geophysical minerals, Debye temperature

I. Introduction

An adequate understanding of thermoelastic properties of geophysical minerals requires the knowledge of temperature dependence of volume thermal expansion at high pressures (Anderson 1995; Stacey and Davis 2004). A multi-step method has been developed by Anderson *et al.* (1995) for estimating the volumes of minerals at high pressures and high temperatures. The study of thermo-physical and thermo-dynamic properties of geophysical minerals is of great importance as far as the validity of high temperature and high pressure equation of state of minerals are concerned. Geophysical minerals such as $MgSiO_3$, MgO , Al_2O_3 , CaO and Mg_2SiO_4 are the major constituents of the Earth's lower mantle and core. Thermal pressure is an important physical quantity playing the central role in the evolution of high temperature equation of states for solids. Various models for the determination of the temperature dependence of P_{th} are critically examined in the light of experimental data. We have studied several formulations for the temperature dependence of thermal pressure demonstrating the inadequacies of the models developed by the earlier researchers.

II. Temperature Dependence Of Volume At High Pressure

Equation of state for a solid describes pressure – volume – temperature relationship expressed as follows: $P(V, T) = P(V, T_0) + \Delta P_{th}$ -----(1)

where $P(V, T)$ is pressure at volume V and temperature T , $P(V, T_0)$ is the isothermal pressure - volume relationship at room temperature, $T_0 = 300$ K and ΔP_{th} is the difference in the values of thermal pressures at temperature T and that at room temperature i.e.

$$\Delta P_{th} = P_{th}(T) - P_{th}(T_0) \text{ -----(2)}$$

Using Maxwell's thermodynamic relationship, equation (2) has been approximately written as

$$\Delta P_{th} = \alpha_0 K_0 (T - T_0) \text{ -----(3)}$$

where α_0 is thermal expansivity and K_0 is the isothermal bulk modulus. "0" refers to the initial value of that parameter. However equation (3) is valid only for those solids which have their Debye temperature very close to room temperature. But some geophysical mineral used in present work have Debye temperature higher than the room temperature. Therefore equation (3) is not valid for these minerals. To investigate the temperature dependence of thermal pressure, we should know the volume dependence of isothermal bulk modulus at constant pressure. The mathematical form of the theory is:

$$(V/V_0) = 1 - 1/A \ln [1 + A/K_0 \{P - \alpha_0 K_0 (T - T_0)\}] \text{ -----(4)}$$

where (V/V_0) is the relative change in volume, V_0 the initial volume, $A = (1 + \delta_0 T)$, δT is the Anderson-Gruneisen parameter, K the isothermal bulk modulus, P the pressure, α_0 is the thermal expansion. At $P=0$, eq. (4) becomes as follows:

$$(V/V_0) = 1 - 1/A \ln [1 - A/K_0 P_{th}] \text{ -----(5)}$$

$$P_{th} = K_0/A [1 - \exp A (1 - V/V_0)] \text{ -----(6)}$$

Nand and Kumar [15] estimated the temperature dependence of thermal pressure for geophysical minerals with the help of volume expansion data, reported by Anderson [3]. They calculated P_{th} with the help of eq. (6) and found that the it is superior to other expressions. By comparing eqs. (3) and (6) , it reveals that $(V/V_0) = 1 - 1/(1+\delta_0 T) \ln [1 - \alpha_0 (T - T_0) / (1+\delta_0 T)]$ -----(7)

Using the values of input parameters from Table 1, we estimated the temperature dependence of volume expansion ratio (V/V_0) with the help of eq. (7) for various minerals. It is found that in most of the cases the predicted values from eq. (7) differ significantly from experimental data. However, for NaCl and KCl, an agreement between theory and experiment can be seen. Thus, eqs. (3) and (6) can used only for those minerals which have Debye's temperature $\theta_D \approx T_0 = 300K$. For other minerals, these expressions cannot be used safely to determine the temperature dependence of thermal pressure. Therefore, the expression given in equation (7) for temperature dependence of thermal pressure cannot be treated as a reliable. At $T = T_0$ (Putting $P = - P_{th}$), the eq. (4) is reduced as follows $(V/V_0) = 1 - 1/A \ln [1 - A/ K_0 P_{th}]$ -----(8)

Now, according to high pressure thermodynamics, the condition $P \rightarrow \infty$ is equivalent to $V \rightarrow 0$. This infinite pressure behavior should be followed by all equation of state (EOS). According to Stacey and Davis [10], the infinite pressure properties are simply equation of state parameters, not observable in any direct sense. However, infinite pressure parameters just as legitimate as physical entities as are zero pressure properties for high pressure materials that do not survive decompression to $P = 0$. It can be seen from eq. (8) that at $P \rightarrow \infty$ the volume goes to acquire negative infinite value, which has no significance. Therefore, the equation of state (EOS) used Nand and Kumar [15] does not follow the constrains made by high pressure thermodynamics. The choice between two K- prime EOS [1] and [7] is not clear-cut to the extent that there may be little reason for making a choice, other than the convenience of use. Generally, if zero pressure properties are known, then the Keane EOS [1] is easy to apply. Therefore in the present study we are applying Keane EOS to study the temperature dependence of thermal pressure. The Keane EOS is expressed as follows:

$$P/ K_0 = K'_0 / K'_\infty{}^2 \{ (V/V_0) - K'_\infty - 1 \} + (K'_0 / K'_\infty - 1) \ln (V/V_0)$$
 -----(9)

Here K'_∞ is the infinite pressure value of K' which is an adjustable parameter. This parameter is a material dependent and remains constant under any conditions such as isothermal, isobaric and adiabatic. At zero pressure, the resultant expression for $P_{th}(T)$ from eq. (9) is obtained as follows (Putting $P = - P_{th}$)

$$P_{th} = K_0 [K'_0 / K'_\infty{}^2 \{ 1 - (V/V_0) - K'_\infty \} - (K'_0 / K'_\infty - 1) \ln (V/V_0)]$$
 -----(10)

We computed the temperature dependence of thermal pressure from eq.(10) for many geophysical minerals. The volume expansion data are calculated from density data, compiled by Anderson [3]. Computed values are also compared with available experimental data. Predicted values from eq. (3) and (6) are also shown in figures for the sake of comparison. It is clear from figures that the eq. (10) reproduces the experimental data very well and superior to eq. (3) and (6). It should be noted that eq. (6) is seriously wrong for those materials which have $\theta_D > T_0$. In fact, for those minerals the eq. (6) should be written as

$$P_{th} = \alpha^* K^* (T - T_0)$$
 -----(11)

where α^* and K^* are the values of α and K at T or near to the Debye temperature. To show the validity of eq. (11), we have also estimated $P_{th}(T)$ from eq. (3) and compared with experimental data in figures. A close agreement between two sets reveals the validity of eq. (11).

III. Figures And Tables

Table 1 - Values of input parameters used in the present study based on experimental data [3]

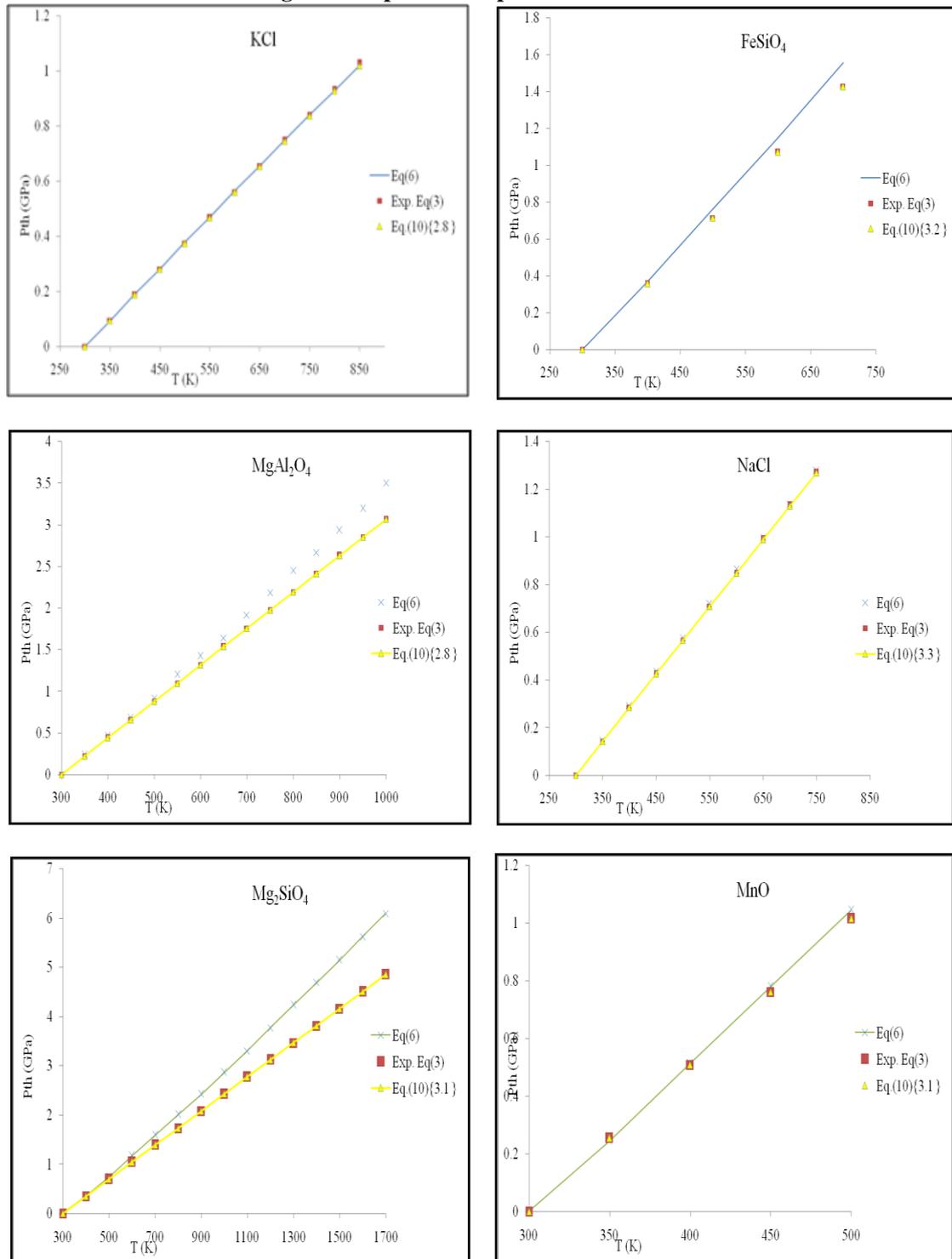
Minerals	$\alpha_0 (10^{-5} K^{-1})$	δ^0_T	$K_0 (G Pa)$	θ_D
Mg ₂ SiO ₄	2.72	3.98	127.3	763
MgAl ₂ O ₄	2.11	7.73	207.9	862
Fe ₂ SiO ₄	2.61	7.34	136.7	511
MnO	3.46	5.96	146.7	534
KCl	11.0	5.84	17	230
NaCl	11.8	5.56	24	304

Table 2 - Comparison between the values of P_{th} (G Pa) for minerals calculated from equations (3), (10) and experimental results given by Anderson [3]

KCl					
T	V/V ₀ Cal. eq. (7)	(P ₀ /P) Exp.	P _{th} (10 ⁹)eq.(6)	P _{th} (10 ⁹) Exp eq.(3)	P _{th} eq.(10){3.1}
300	1.0000	1.0000	0.0000	0.0000	0.0000
350	1.0056	1.0056	0.0931	0.0935	0.0935
400	1.0114	1.0117	0.1918	0.1870	0.1870
450	1.0175	1.0175	0.2797	0.2805	0.2804
500	1.0238	1.0243	0.3804	0.3740	0.3737
550	1.0305	1.0307	0.4705	0.4675	0.4668
600	1.0374	1.0377	0.5649	0.5610	0.5598

650	1.0447	1.0448	0.6561	0.6545	0.6524
700	1.0523	1.0526	0.7507	0.7480	0.7447
750	1.0604	1.0605	0.8418	0.8415	0.8365
800	1.0690	1.0685	0.9294	0.9350	0.9277
850	1.0781	1.0772	1.0194	1.0285	1.0182
Fe₂SiO₄					
T	V/V₀ Cal. eq. (7)	(P₀/P) Exp.	P_{th}(10⁹)eq.(6)	P_{th}(10⁹) Exp eq.(3)	P_{th}eq.(10){3.2}
300	1.0000	1.0000	0.0000	0.0000	0.0000
400	1.0026	1.0027	0.3696	0.3568	0.3568
500	1.0053	1.0057	0.7628	0.7136	0.7135
600	1.0081	1.0087	1.1486	1.0704	1.0701
700	1.0109	1.0120	1.5560	1.4271	1.4265
MgAl₂O₄					
T	V/V₀ Cal. eq. (7)	(P₀/P) Exp.	P_{th}(10⁹)eq.(6)	P_{th}(10⁹) Exp eq.(3)	P_{th}eq.(10){2.8}
300	1.0000	1.0000	0.0000	0.0000	0.0000
350	1.0011	1.0011	0.2317	0.2193	0.2193
400	1.0021	1.0022	0.4616	0.4387	0.4387
450	1.0032	1.0034	0.6898	0.6580	0.6580
500	1.0043	1.0045	0.9163	0.8773	0.8773
550	1.0054	1.0059	1.1970	1.0967	1.0965
600	1.0065	1.0070	1.4196	1.3160	1.3157
650	1.0076	1.0082	1.6405	1.5353	1.5349
700	1.0088	1.0096	1.9143	1.7547	1.7540
750	1.0099	1.0110	2.1855	1.9740	1.9731
800	1.0111	1.0125	2.4541	2.1933	2.1920
850	1.0122	1.0136	2.6670	2.4127	2.4109
900	1.0134	1.0150	2.9310	2.6320	2.6297
950	1.0146	1.0165	3.1923	2.8513	2.8483
1000	1.0158	1.0182	3.5026	3.0707	3.0669
NaCl					
T	V/V₀ Cal. eq. (7)	(P₀/P) Exp.	P_{th}(10⁹)eq.(6)	P_{th}(10⁹) Exp eq.(3)	P_{th}eq.(10){3.3}
300	1.0000	1.0000	0.0000	0.0000	0.0000
350	1.0060	1.0061	0.1425	0.1416	0.1416
400	1.0123	1.0127	0.2917	0.2832	0.2832
450	1.0188	1.0194	0.4363	0.4248	0.4246
500	1.0256	1.0261	0.5765	0.5664	0.5660
550	1.0328	1.0335	0.7220	0.7080	0.7072
600	1.0403	1.0410	0.8625	0.8496	0.8481
650	1.0482	1.0486	0.9982	0.9912	0.9887
700	1.0565	1.0568	1.1377	1.1328	1.1289
750	1.0653	1.0656	1.2802	1.2744	1.2685
Mg₂SiO₄					
T	V/V₀ Cal. eq. (7)	(P₀/P) Exp.	P_{th}(10⁹)eq.(6)	P_{th}(10⁹) Exp eq.(3)	P_{th}eq.(10){3.1}
300	1.0000	1.0000	0.0000	0.0000	0.0000
400	1.0027	1.0028	0.3541	0.3463	0.3463
500	1.0055	1.0059	0.7441	0.6925	0.6925
600	1.0083	1.0094	1.1689	1.0388	1.0388
700	1.0112	1.0129	1.5892	1.3850	1.3851
800	1.0141	1.0164	2.0052	1.7313	1.7314
900	1.0170	1.0199	2.4167	2.0775	2.0777
1000	1.0200	1.0238	2.8607	2.4238	2.4240
1100	1.0230	1.0278	3.2995	2.7700	2.7704
1200	1.0261	1.0320	3.7689	3.1163	3.1168
1300	1.0292	1.0363	4.2323	3.4626	3.4632
1400	1.0324	1.0407	4.6895	3.8088	3.8097
1500	1.0356	1.0451	5.1407	4.1551	4.1562
1600	1.0389	1.0499	5.6199	4.5013	4.5028
1700	1.0422	1.0547	6.0920	4.8476	4.8494
MnO					
T	V/V₀ Cal. eq. (7)	(P₀/P) Exp.	P_{th}(10⁹)eq.(6)	P_{th}(10⁹) Exp eq.(3)	P_{th}eq.(10){3.1}
300	1.0000	1.0000	0.0000	0.0000	0.0000
350	1.0017	1.0017	0.2445	0.2538	0.2538
400	1.0035	1.0035	0.5138	0.5076	0.5076
450	1.0053	1.0054	0.7805	0.7614	0.7613
500	1.0071	1.0073	1.0448	1.0152	1.0151

Figure: Temperature dependence of minerals



IV. Conclusion

From figures it is clear that our results calculated from equations (6) and (10) for geophysical minerals under study give close agreement with the experimental values of thermal pressure at different temperature. It should be emphasized that the modification considered in the present study in the form of equations (7) and (10) are of fundamental importance in the theory of thermal expansivity of solids. The present study provides the way to understand thermo-elastic property of solid by using a formulation which is valid up to extreme compression limit.

References

- [1]. Keane: Aust. J. Phys., 1954, 7, p 322.
- [2]. O.L. Anderson, H. Odd and D.G. Isaak: Geophys. Res. Lett., 1992, 19, p 1987.
- [3]. O.L. Anderson: Equations of State of Solids for Geophysics and Ceramic Sciences, Oxford University Press, New York, 1995.
- [4]. M. Kumar: Physics B. Condensed Matter, 1995, 212, p 391.
- [5]. M. Kumar: Phys. Stat. Solidi (b), 1996, 195, p 303.
- [6]. J. Shanker, S.S. Kushwah and P. Kumar: Physica B. Condensed Matter, 1997, 233(1), p 78.
- [7]. F.D. Stacey: Phys. Earth Planet Inter., 2001, 12, p 179.
- [8]. B.P. Singh, S.K. Srivastava and K. Dinesh: Physica B. Condensed Matter, 2004, 349, p 401.
- [9]. K. Sushil, K. Arunesh, P.K. Singh and B.S. Sharma: Physica B. Condensed Matter, 2004, 352(1), p 134.
- [10]. F.D. Stacey and P.M. Davis, Phys. Earth Planet Inter., 2004, 142, p 137.
- [11]. J. Kung and R. C. Liebermann: Phys. Earth Planet Inter., 2004, 143, p 559.
- [12]. J. Garai: J. Applied Phys., 2007, 101, p 023514.
- [13]. S. Digpratap, K. Rakesh and K. Arunesh: Indian J. Phys., 2007, 45, p 657.
- [14]. S.K. Srivastava, P. Sinha, B.S. Khushwah: J. Phys. Chem. Solids, 2009, 70(2), p 356.
- [15]. G. Nand and M. Kumar: Indian J. Phys., 2010, 84, p 459.
- [16]. P.K. Singh: Indian J. Pure and Applied Physics, 2011, p 829.
- [17]. S.K. Srivastava and P. Sinha: J. Pure and Applied Physics, 2011, 49, p 195.
- [18]. M. Singh, H. Narayan and M. Kumar: American Journal of Condensed Matter Physics 2012, 2(4), p88-92.
- [19]. Orson L. Anderson, Donald L. Isaak and Hitoshi Oda: Journal of Geophysical Research: Solid Earth, 2012, Volume 96, Issue B11, p 18037–18046.