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Analysis Of Holzapfel AP2 Equation Of State And Isothermal Bulk Modulus For Binary Solids At High Pressures

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Abstract

In this study, we have determined pressure – volume relationship, bulk modulus and its pressure derivatives for binary solids viz., NaCl, NaF and MgO under high pressure and high temperature conditions. We have used the Holzapfel AP2 equation of state (EOS) which has a fundamental physical origin based on the Thomas – Fermi electron gas model in the limit of extreme compression. To analyze the behavior at extreme compression, Stacey's infinite pressure relation $\lim_{P\to\infty}(P/K_T) = 1/K_T^{\infty}$ is utilized. This constraint models how the pressure to bulk modulus ratio approaches a finite limit $1/K_T^{\infty}$ under extreme compression. The computed plots of P/K_T versus $1/K_T'$ across different isotherms at selected temperatures shows strong alignment with Stacey's relation confirms the physical validity and stability of the Holzapfel AP2 EOS for binary solids under high pressures and high temperature conditions.

Keywords: P-V-T relationships,Isothermal bulk modulus, Holzapfel AP2 EOS, Binary solids

Introduction

Understanding the thermodynamic and thermoelastic properties of solids under extreme pressure conditions is fundamental to condensed matter physics, geophysics and material science [1]. Equation of state (EOS) provides critical relationship models linking volume (V), pressure (P) and temperature (T). Binary solids such as alkali halides (NaCl, NaF) and alkaline earth oxide (MgO) for which the thermoelastic properties are investigated in the present study are important technological materialswidely utilized in optical components, high temperature ceramic insulation and radiation detectors due to their wide crystal stability. NaCl andNaF do not exhibit any phase transition up to about 30 Gpa [2, 3] and 23GPa [4]. For MgO, the B1 – B2 phase transition boundary starts at about 500GPa at and T = 0and goes up to the B1-B2 liquid triple point at ~(250 GPa, 8500K) [5, 6]. In case of NaF we report the results up to 28 GPa which is higher than the B1 – B2 phase transition pressure ~ 23GPa [4]. Thus behavior of NaF definitely concerns both the B1 and B2 structures of NaF. The melting temperature T_m for MgO at ambient pressure is nearly 3000K [7] which is substantially higher than $T_m = 1074K$ for NaCl and $T_m = 1261K$ for NaF [1,8]. The Debye temperature (θ_D) for NaCl, NaF and MgO are respectively 304K, 470K and 945K [1, 7, 8]. It should be mentioned that NaCl is an important representative material for ionic solid [1,9, 10]. Such a wide range pressure P and temperature T for these binary solids make it suitable material to be used as a high temperature – pressure calibrant for experimental work [11]. Reliable pressure – volume (P –V) data are required along different isotherms at high temperatures for a material to be used as a pressure scale. A number of equations of state models have been constructed by Dorogokupets and Oganov [6, 12 - 14] for determining P-V-T results in case of several solids including binary solids. They have been used various equations of state such as Birch EOS [15], Vinet EOS [16] and the Holzapfel AP2 EOS[17]. It has been found by Belonoshko et al. [18]

that the Holzapfel AP2 EOS is consistent with the ab initio molecular dynamics results and gives a correct Thomas – Fermi limit for materials at extreme compression [19, 20].

In the present study , we conducted a systematic computation of pressure P, isothermal bulk modulus K_T and its pressure derivative $K_T'$for NaCl, NaF and MgO along various isotherms at different temperatures, analyzing their validation against Stacey's extreme pressure expolation framework [21, 22].

Method of analysis:

The Holzapfel AP2 EOS can be written as [17]

$$P = 3K_0 x^{-5}(1-x)[1+C_2 x(1-x)]\exp[C_0(1-x)] \quad (1)$$

where $x = (V/V_0)^{1/3}$, K_0 is the value of bulk modulus K at pressure P=0, and

$$C_0 = -\ln\left(\frac{3K_0}{P_{FG0}}\right) \quad (2)$$

Here P_{FG0} is the Fermi gas pressure given below

$$P_{FG0} = a_{FG}\left(\frac{Z}{V_0}\right)^{5/3} \quad (3)$$

where a_{FG} = 0.02337 GPanm^5, and Z is the number of electrons multiplied by Avogadro per atomic volume V. In case of NaCl, NaF and MgO, we have Z = 28, 20 and 20 respectively. These are to be multiplied by the Avogadro number when V_0 is given in the units of $cm^3/mole$. The constant C_2 in equation (1) is related to K_0', the value of $K' = \partial K/\partial P$ at $P = 0$, as follows:

$$C_2 = \frac{3}{2}(K_0' - 3) - C_0 \quad (4)$$

P-V relationship along different isotherms at selected temperatures for these binary solids has been determined by using equation (2). The required input data for V_0, K_0 and K_0' at different temperatures have been taken from the Literature [1, 8, 23-28] and given in the Tables 1, 2 and 3 along with the values of P_{FG0}, C_0 and C_2 calculated from equations (2 – 4). Values of input parameters are temperature dependent, and we have used appropriate values corresponding to each temperature. It should be emphasized that equation (1) yield the correct Thomas – Fermi limit $(K_\infty' = 5/3)$ in the limit of extreme compression$(V \to 0)$. This method has been used successfully by earlier workers [26, 29, 30].

In addition to P-V isotherms we have also calculated higher derivative thermoelastic properties such as the bulk modulus and its pressure derivative. The expressions for the bulk modulus K and its pressure derivative $K' = \partial K/\partial P$ are obtained using the following relationships

$$K_T = -V\left(\frac{\partial P}{\partial V}\right)_T \quad (5)$$

$$K_T' = \left(\frac{\partial K_T}{\partial P}\right)_T$$

$$K_T' = \left[-1 - \frac{V^2\left(\frac{\partial^2 P}{\partial V^2}\right)}{V\left(\frac{\partial P}{\partial V}\right)_T}\right] \quad (6)$$

Now using equations (1), (5) and (6), we have determined the results for pressure P, isothermal bulk modulus K_T and pressure derivative of bulk modulus K_T' for these binary solids given in Tables 4-12 respectively.

It should be noted that any thermodynamic formulation or more precisely any equation of state is physically acceptable only when it satisfies the following conditions at extreme compression [21, 22]. 1.

The volume V of a material tends to zero only at infinite pressure and vice versa, 2. The bulk modulus $K_T'$of a material tends to infinity as the pressure $P \to \infty$, and 3. P and K_T' both tend to infinity in the limit $V \to 0$, but their ratio (P/K) remain finite . it was found by Stacey [31, 32]

$$\left(\frac{P}{K}\right)_{\infty} = \frac{1}{K_{\infty}'} \qquad (7)$$

Where K_{∞}' is the value of $K' = \partial K/\partial P$, the pressure derivative of the bulk modulus at infinite pressure. Stacey and Davis [21] found that above equaton is satisfied by all equation of state with K_{∞}' greater than zero. A positive finite value of K_{∞}' ensure that conditions (1) and (2) given above are satisfied.

Stacey[32] has made an effective use of equation (7) by developing a reciprocal K-primed EOS which can be written as follows

$$\frac{1}{K'} = \frac{1}{K_0'} + \left(1 - \frac{K_{\infty}'}{K_0'}\right)\frac{P}{K} \qquad (8)$$

Equation (8) shows a linear relationship between P/K and $1/K'$.

Results and discussion:

It is found that the results for pressure for pressure volume relationships (Tables 4-6), isothermal bulk modulus K (Tables 7-9) and pressure derivative of bulk modulus K' computed in the present study are in the close agreement with the available data [3, 33 - 39]. We note from equation Tables 4-6 that pressure decreases with the increase in temperature for a given value of change in volume. Thus at higher temperatures, the material becomes softer, i.e. it can be compressed by the same amount with the application of lower pressure as the temperature is increased. This is also evident that from Table 7-9 that values of bulk modulus K increase with volume compression $(1 - V/V_0)$ and decrease with increase in temperatures. The variation of bulk modulus with the pressure is similar to that of melting temperature T_M with pressure. In case of binary solids viz., NaCl, NaF and MgO , the bulk modulus and T_M both increase non-linearly with the increase in pressure [3, 40]. The decrease in bulk modulus at high temperature to a critical extent is responsible for mechanical collapse of the structure resulting into melting. At high pressures, the rate of decreasing bulk modulus with temperature is reduced substantially, higher values of temperatures are required to lower the bulk modulus down to a value causing mechanical instability related to melting. This explains why melting temperature increases with the increase in pressure values of K' has also been computed for NaCl, NaF and MgO in Table 10-12 respectively. it should be mentioned that K' increases with the increase in temperature and decreases with the increase in pressure.More precisely any equation of state is physically acceptable only when it satisfies the following conditions at extreme compression [21, 22]. 1. The volume V of a material tends to zero only at infinite pressure and vice versa, 2. The bulk modulus K_T' of a material tends to infinity as the pressure $P \to \infty$, and 3. P and K_T' both tend to infinity in the limit $V \to 0$, but their ratio (P/K) remain finite. Equations (1), (5) and (6) given by Holzapfel [17] consider in the present study satisfy the condition given above.

We observed from figures 1-3 that in the limit of extremely high pressure the plots corresponding to different temperature appear to merge into each-other. This would imply that K_{∞}', the value of K' in the limit of infinity pressure becomes independent of temperatures . This is an important result found by Stacey and Davis from the fundamental considerations based on thermodynamics of solids.

Conclusions:

We have thus used the Holzapfel AP2 EOS to evaluate the pressure-volume – temperature relationships of binary solids viz., NaCl. NaF and MgO under high pressure and high temperature conditions. These calculations show that as temperature rises, materials soften and require less pressure for volume compression. Furthermore, at extreme compression, the $1/K_{\infty}'$versus P/K plots across different isotherms appear to merge into each other. This behavior adheres the fundamental considerations based on thermodynamics of solids given by Stacey and Davis.

TABLE 1

Values of input parameters for NaCl used in computations are from [24, 26, 27].

T (K)	K_0 (GPa)	K_0'	$V_0 = V(T, 0)$ $(cm^3/mole)$	P_{FGO} (GPa)	C_0	C_2
300	23.85	5.35	27.01	1065.62	2.70	0.83
450	21.31	5.59	27.52	1033.05	2.77	0.99
600	18.85	5.82	28.10	997.87	2.87	1.22
750	16.53	6.07	28.56	960.19	2.97	1.58
900	14.12	6.26	29.52	919.39	3.08	2.02
1050	11.85	6.53	30.42	874.39	3.22	2.57

TABLE 2

Values of input parameters for NaF used in computations are from references [8, 23].

T(K)	K_0(GPa)	K_0'	$V_0 = V(T.0)$ $(cm^3/mole)$	P_{FGO} (GPa)	C_0	C_2
300	46.5	5.25	14.98	1625	2.46	0.92
450	42.6	5.33	15.28	1572	2.51	0.98
600	38.7	5.42	15.45	1544	2.59	1.04
750	34.8	5.52	15.75	1495	2.66	1.12
900	30.9	5.63	16.08	1444	2.75	1.20
2500	26.9	5.76	16.45	1390	2.84	1.29
3000	23.0	5.92	16.90	1329	2.96	1.42

TABLE 3

Values of input parameters for MgO used in computations are from references [1, 25, 28].

T(K)	K_0(GPa)	K_0'	$V_0 = V(T.0)$ $(cm^3/mole)$	P_{FGO} (GPa)	C_0	C_2
300	162	4.15	11.24	2623	1.69	0.04
500	156	4.21	11.33	2588	1.71	0.10
1000	141	4.36	11.57	2499	1.78	0.26
1500	126	4.53	11.84	2405	1.85	0.44
2000	109	4.74	12.15	2304	1.96	0.65
2500	94.0	4.95	12.49	2200	2.06	0.86
3000	79.0	5.16	12.86	2096	2.18	1.06

TABLE 4

Values of pressure P (GPa) for NaCl computed using equation (1) at different temperatures.

V/V_0	P (GPa)					
	T =300K	450K	600K	750K	900K	1050K
1.00	0	0	0	0	0	0
0.95	1.41	1.26	1.12	0.99	0.85	0.72
0.90	3.25	2.94	2.63	2.34	2.01	1.71
0.85	5.82	5.29	4.76	4.25	3.68	3.15
0.80	9.38	8.57	7.75	6.60	6.05	5.22
0.75	14.33	13.17	11.98	10.81	9.45	8.21
0.70	20.87	19.30	17.63	16.0	14.05	12.99
0.65	30.46	28.32	26.04	23.75	21.33	18.44

TABLE 5

Values of pressure P (GPa) for NaF computed using equation (1) at different temperatures.

V/V_0	P (GPa)						
	T =300K	450K	600K	750K	900K	1050K	1200K
1.00	0	0	0	0	0	0	0
0.95	2.73	2.51	2.28	2.05	1.83	1.60	1.38
0.90	6.31	5.80	5.29	4.60	4.27	3.75	3.23
0.85	11.23	10.36	9.47	8.58	7.68	6.77	5.86
0.80	18.07	16.68	15.29	13.88	12.45	11.02	9.57
0.75	27.52	25.46	23.38	21.29	19.15	17.00	14.82

TABLE 6

Values of pressure P (GPa) for MgO computed using equation (1) at different temperatures.

	P (GPa)						
V/V_0	T=300K	500K	1000K	1500K	2000K	2500K	3000K
1.00	0	0	0	0	0	0	0
0.95	9.27	8.94	8.11	7.28	6.33	5.49	4.64
0.90	20.83	20.11	18.32	16.5	14.43	12.57	10.68
0.85	36.11	34.9	31.92	28.88	25.38	22.22	18.97
0.80	56.37	54.58	50.09	45.51	40.22	35.39	30.37
0.75	83.38	80.84	74.5	67.98	60.39	53.42	46.09
0.70	117.66	114.22	105.67	96.82	86.47	76.87	66.66
0.65	165.96	161.34	149.88	137.91	123.85	110.68	96.5
0.60	228.41	222.36	207.37	191.6	172.99	155.35	136.14

TABLE 7

Values of isothermal bulk modulus K_T (GPa) for NaCl obtained using equation (5) at different temperatures.

V/V_0	K_T (GPa)					
	T=300K	450K	600K	750K	900K	1050K
1.00	23.85	21.31	18.85	16.53	14.12	11.85
0.95	31.06	27.97	25.08	22.25	19.17	16.27
0.90	39.87	36.45	32.78	29.34	25.46	21.81
0.85	51.33	47.33	42.87	38.69	33.79	29.17
0.80	66.31	61.4	56.19	51.08	44.87	39.03
0.75	86.06	79.78	73.89	67.62	59.72	52.21
0.70	110.88	104.06	96.33	88.67	78.7	69.32
0.65	145.61	136.66	127.95	118.47	105.66	93.63

TABLE 8

Values of bulk modulus K_T (GPa) for NaF obtained by equation (5) at different temperatures.

	K_T (GPa)						
V/V_0	T=300K	450K	600K	750K	900K	1050K	1200K
1.00	46.5	42.6	38.7	34.8	30.9	26.9	23.0
0.95	60.3	55.4	50.4	45.6	40.7	35.8	30.8
0.90	77.0	70.0	65.0	58.9	52.8	46.6	40.4
0.85	98.7	91.25	83.8	76.3	68.6	60.9	53.0
0.80	126.8	117.6	108.4	99.0	89.4	79.6	69.8
0.75	163.8	152.3	140.8	128.9	116.8	104.5	92.0

TABLE 9

Values of bulk modulus K_T (GPa) for MgO obtained using equation (5) at various temperatures for MgO.

	K_T (GPa)						
V/V_0	T=300K	500K	1000K	1500K	2000K	2500K	3000K
1.00	162.00	156.00	141.00	126.00	109.00	94.00	79.00
0.95	199.38	192.48	175.24	157.83	137.90	120.08	101.92
0.90	243.61	235.69	215.94	195.81	172.57	151.50	129.67
0.85	299.31	290.18	270.01	244.01	216.77	191.73	165.37
0.80	369.92	359.34	333.00	305.61	273.5	243.58	211.60
0.75	460.14	447.78	417.10	384.88	346.83	310.90	271.87
0.70	570.22	555.80	520.15	482.32	437.34	394.30	346.86
0.65	719.68	702.61	660.60	615.57	561.58	509.00	450.63
0.60	906.25	886.04	836.57	782.86	718.31	654.71	582.54

TABLE 10

Values of Pressure derivative of bulk modulus K_T' calculated by equation (6) at various temperatures for NaCl

V/V_0	K_T'					
	T =300K	450K	600K	750K	900K	1050K
1.00	5.35	5.59	5.82	6.07	6.26	6.51
0.95	4.94	5.14	5.31	5.50	5.66	5.85
0.90	4.62	4.78	4.92	5.09	5.21	5.36
0.85	4.34	4.48	4.60	4.73	4.83	4.97
0.80	4.10	4.21	4.32	4.43	4.52	4.63
0.75	3.89	3.99	4.08	4.17	4.25	4.35
0.70	3.71	3.79	3.87	3.96	4.02	4.11
0.65	3.54	3.62	3.69	3.76	3.82	3.89

TABLE 11

Values of pressure derivative of bulk modulus K_T' for NaF calculated using equation (6) at various temperatures for NaF.

	K_T'						
V/V_0	T=300K	450K	600K	750K	900K	1050K	1200K
1.00	5.25	5.33	5.42	5.52	5.63	5.76	5.92
0.95	4.86	4.92	4.98	5.07	5.17	5.26	5.40
0.90	4.54	4.59	4.65	4.72	4.80	4.88	5.00
0.85	4.26	4.30	4.36	4.43	4.49	4.56	4.66
0.80	4.03	4.06	4.11	4.17	4.22	4.29	4.38
0.75	3.82	3.86	3.90	3.94	3.99	4.05	4.12

TABLE 12

Values of pressure derivative of bulk modulus K_T' for MgO calculated using equation (6) at various temperatures for MgO

	K_T'						
V/V_0	T=300K	500K	1000K	1500K	2000K	2500K	3000K
1.00	4.13	4.21	4.36	4.53	4.74	4.95	5.16
0.95	3.90	3.95	4.11	4.24	4.42	4.60	4.77
0.90	3.71	3.77	3.84	4.01	4.15	4.30	4.45
0.85	3.55	3.60	3.70	3.80	3.93	4.05	4.18
0.80	3.39	3.44	3.53	3.62	3.73	3.84	3.94
0.75	3.26	3.31	3.38	3.45	3.55	3.64	3.74
0.70	3.13	3.18	3.24	3.31	3.40	3.48	3.57
0.65	3.02	3.06	3.12	3.2	3.26	3.33	3.40
0.60	2.92	2.96	3.01	3.06	3.13	3.19	3.26

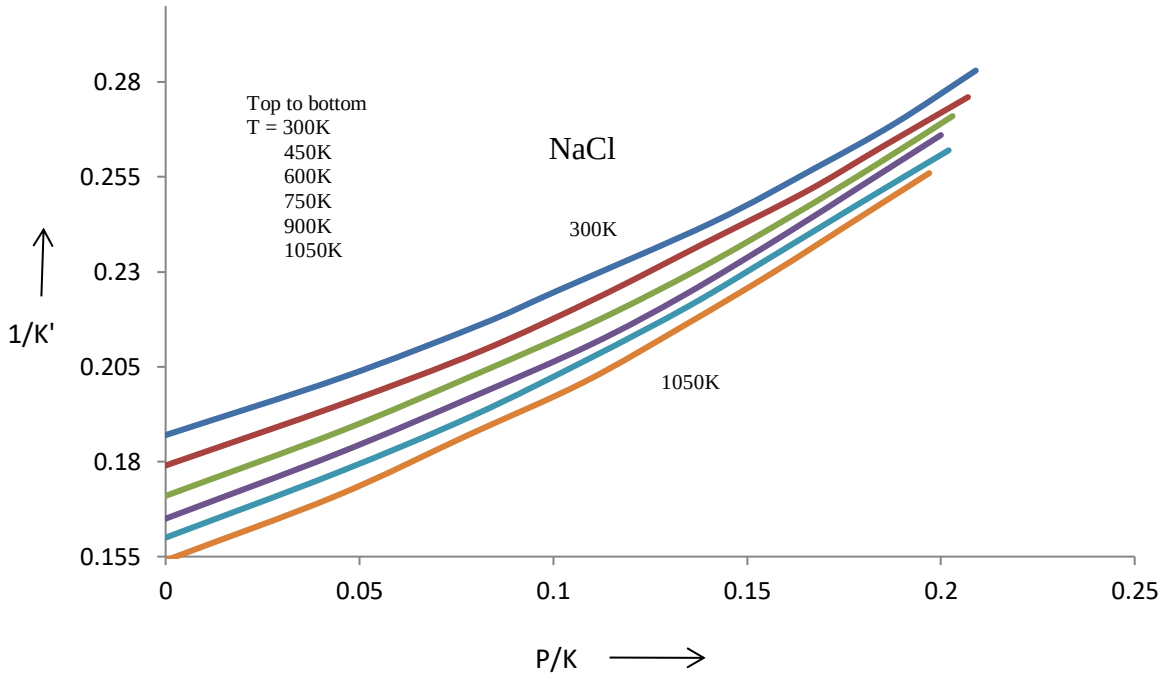

Figure 1: Plots$1/K'$ versus P/K for NaCl along different isotherms at selected temperatures by using Holzapfel AP2 EOS.

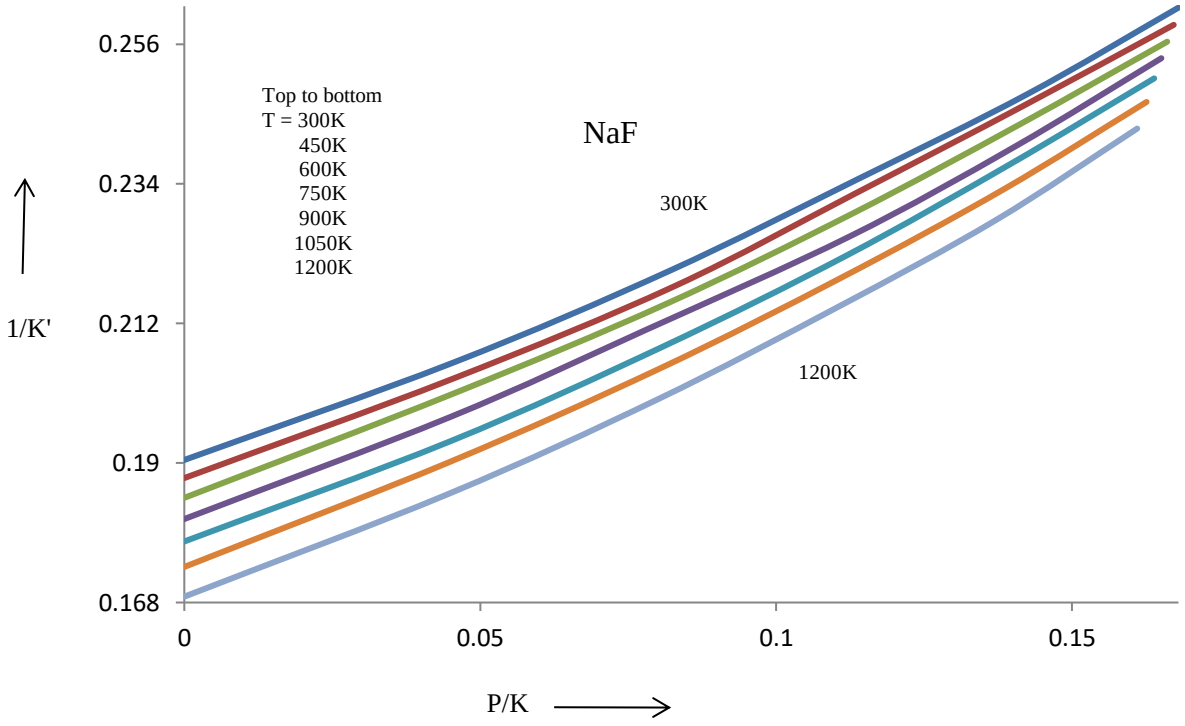

Figure 2: Plots of $1/K'$ versus P/K for NaF along different isotherms at selected temperatures by using Holzapfel AP2 EOS.

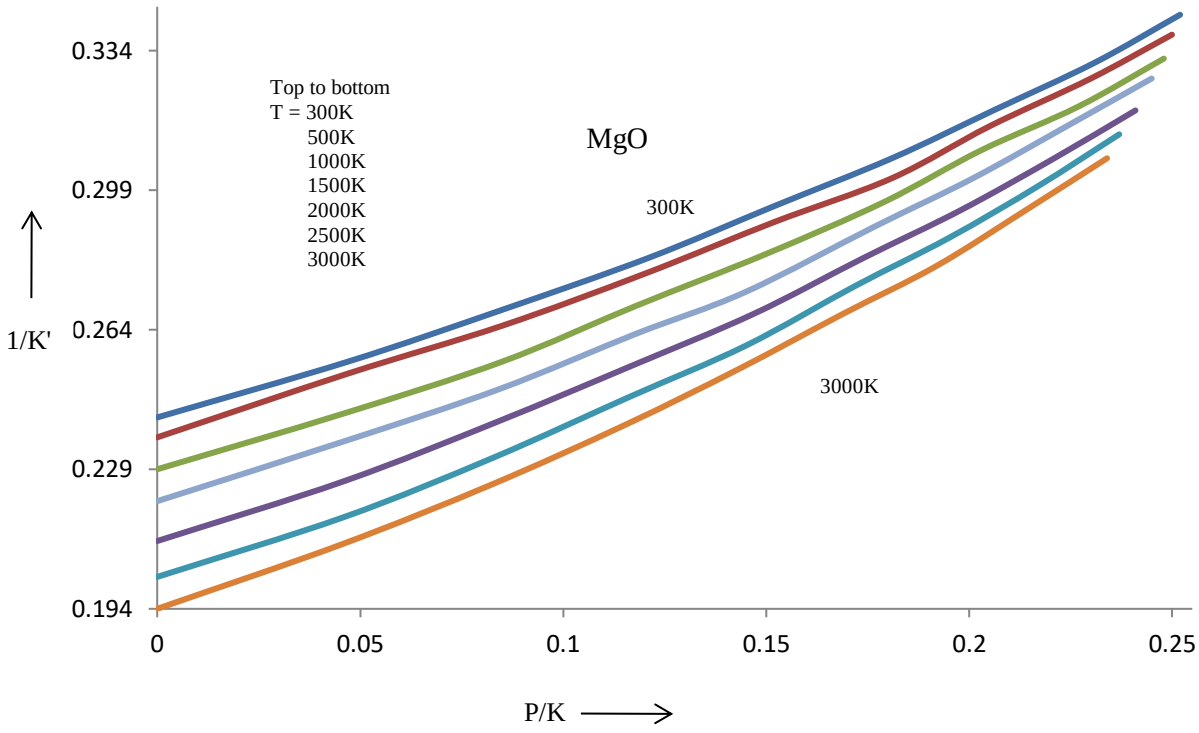

Figure 3: Plots of $1/K'$ versus P/K for MgO along different isotherms at selected temperatures by using Holzapfel AP2 EOS.

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