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An equation of state applied to 50 solids: II

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Abstract. The equation of state suggested by the authors has been applied to 50 solids. The maximum pressure range and the minimum pressure range used in the present study are 0–4500 kbar and 0–100 kbar, respectively. Very good agreement is found between the calculated and experimental values of $V(P, T_0)/V(0, T_0)$ for all the solids.

In general, an equation of state of matter is a relation between P, V and T. However, the relation between P and V, under a specific thermodynamic condition in particular is also taken to be an equation of state. If it is so, then a variety of equations of state in current use can either be expressed in or be derived from a power series expansion of the form

$$X = \sum_{i=0}^{n} A_i Y^i \tag{1}$$

where X and Y are two variables under a specific thermodynamic condition. The various forms of X and Y used in the literature have been listed by Mao (1970) and Macdonald (1969). If all the A_i coefficients are known, then all the equations of state under the same thermodynamic condition would be identical. In reality, only a limited number of parameters are determined. Hence, it becomes essential and necessary to truncate the series. Thus, it is the truncation which

(i) gives various orders of approximation,
(ii) differentiates one equation of state from the other and
(iii) introduces physically implausible implications in some instances.

Therefore, the validity of a particular equation of state, having a number of parameters, can only be judged by comparison with the experimental data over the specified pressure range. However, the smaller the number of the adjustable parameters required for the highest pressure range, the better is the equation of state. Note that the equations of state listed by Mao (1970) and Macdonald (1969) may be used up to a pressure of 100 kbar or so.

Therefore, the purpose of the present paper is to seek an equation of state which can be applied in the low-pressure as well as in the high-pressure region without using

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Table 1. The values of $B_T(0, T_0)$, $B'_T(0, T_0)$ and Z along with the root mean square deviation at $T_0 = 25$ °C. All experimental data for $V(P, T_0)/V(0, T_0)$ are taken from Kennedy and Keeler (1972) except for Al (Rice *et al* 1958) and CsI and Xe (Zisman *et al* 1985).

Sample	Solid	Pressure range (kbar)	$B_T(0, T_0)$ (kbar)	$B'_T(0, T_0)$	Z ($\times 10^{-4}$ kbar^{-1})	RMSD (of $V(P, T_0)/V(0, T_0)$) ($\times 10^{-4}$)	Reference
1	Cu	0–4500	1431.93	4.332	1.234	5.22	Present work
			1625.35	4.426			Vaidya and Kennedy (1970)
2	Mo	0–3500	2703.69	3.722	1.326	2.77	Present work
			2660.37	11.963			Vaidya and Kennedy (1970)
3	Zn	0–2500	622.70	4.936	2.002	4.96	Present work
			597.91	4.880			Vaidya and Kennedy (1970)
4	Ag	0–2000	1075.48	5.113	1.989	3.37	Present work
			1208.83	2.484			Vaidya and Kennedy (1970)
5	Pt	0–2000	2821.74	4.872	1.438	2.76	Present work
			2760.0				Brandes (1983)
6	Ti	0–2000	998.68	3.255	3.151	3.95	Present work
			1084.0				Brandes (1983)
7	Ta	0–1800	1989.68	3.581	2.326	2.91	Present work
			2056.9	2.759			Vaidya and Kennedy (1970)
8	Au	0–1800	1859.51	4.776	1.868	4.53	Present work
			1710.0				Brandes (1983)
9	Pd	0–1600	1970.26	4.831	1.783	3.23	Present work
			1870.0				Brandes (1983)
10	Zr	0–1400	954.06	2.633	3.975	3.15	Present work
			898.0				Brandes (1983)
11	Cr	0–1200	1907.22	4.754	2.901	6.90	Present work
			1602.0				Brandes (1983)
12	Co	0–1200	1968.48	4.180	2.868	2.59	Present work
			1815.0				Brandes (1983)
13	Ni	0–1200	1891.79	4.542	2.248	2.75	Present work
			1904.8	20.157			Vaidya and Kennedy (1970)
14	Al_2O_3	0–1200	2521.11	3.789	2.011	2.82	Present work
			2504.1	4.00			Anderson (1966)
15	Nb	0–1000	1676.74	4.034	5.645	19.4	Present work
			1703.0				Brandes (1983)
16	Cd	0–1000	513.23	5.106	3.616	3.67	Present work
			447.6	7.307			Vaidya and Kennedy (1970)
17	Al	0–1000	789.0	3.320	9.00	7.34	Present work
			778.77	3.165			Vaidya and Kennedy (1970)
18	Th	0–1000	532.34	3.701	4.851	4.10	Present work
			540.00				Brandes (1983)
19	V	0–1000	1589.66	3.585	2.441	2.94	Present work
			1580.0				Brandes (1983)
20	In	0–900	403.52	4.756	5.059	14.0	Present work
			390.77	5.239			Vaidya and Kennedy (1970)
21	MgO	0–900	1487.08	5.519	3.587	2.44	Present work
			1691.80	3.95			Anderson (1966)
22	Brass	0–850	1179.65	4.495	3.528	3.04	Present work
23	Be	0–800	1200.12	3.469	4.732	2.46	Present work
			1100.0				Brandes (1983)
24	LiF	0–800	634.12	4.432	4.888	2.91	Present work
			627.85	6.818			Vaidya and Kennedy (1971)
25	Pb	0–750	449.70	4.696	5.097	3.28	Present work
			399.82	6.76			Vaidya and Kennedy (1970)
26	Sn	0–600	442.16	4.900	5.294	2.96	Present work
			549.20	3.651			Vaidya and Kennedy (1970)
27	Mg	0–550	350.05	3.684	8.699	3.41	Present work
			344.20	4.16			Anderson (1966)
28	CsBr	0–550	224.19	3.575	10.18	3.65	Present work
			143.97	5.32			Vaidya and Kennedy (1971)
29	CsI	0–532	111.31	6.084	32.67	40.5	Present work

Table 1 *continued.*

Sample	Solid	Pressure range (kbar)	$B_T(0, T_0)$ (kbar)	$B'_T(0, T_0)$	Z ($\times 10^{-4}$ kbar^{-1})	RMSD (of $V(P, T_0)/V(0, T_0)$) ($\times 10^{-4}$)	Reference
			118.9	5.93			Huang and Ruaff (1984)
30	Xe	0–524	15.12	5.708	23.98	35.0	Present work
			26.5	7.69			Asaumi (1984)
31	Ca	0–360	196.02	2.397	19.84	4.43	Present work
			186.82	2.524			Vaidya and Kennedy (1970)
32	Tl	0–340	358.89	5.142	8.861	2.64	Present work
			366.03	4.795			Vaidya and Kennedy (1970)
33	LiI	0–280	330.32	2.393	15.69	3.13	Present work
			168.35	4.32			Vaidya and Kennedy (1971)
34	LiBr	0–240	222.75	4.172	14.66	3.05	Present work
			242.7	3.50			Vaidya and Kennedy (1971)
35	NaBr	0–240	211.50	3.974	15.90	3.37	Present work
			203.1	4.19			Vaidya and Kennedy (1971)
36	NaI	0–240	200.88	3.594	18.52	2.63	Present work
			151.0	4.15			Vaidya and Kennedy (1971)
37	KF	0–240	125.28	4.809	7.201	4.43	Present work
38	RbF	0–240	153.28	4.265	16.70	3.35	Present work
39	LiCl	0–220	330.15	3.765	8.019	2.64	Present work
			318.5	3.36			Vaidya and Kennedy (1971)
40	Li	0–200	107.62	3.274	26.43	2.98	Present work
			119.8	3.55			Felice and Trivisonno (1977)
41	Na	0–200	61.77	3.43	29.16	5.15	Present work
			62.0	3.50			Vaidya *et al.* (1971)
42	KI	0–180	96.15	4.042	23.74	3.40	Present work
43	RbI	0–180	96.80	4.060	24.89	3.15	Present work
			106.40	5.05			Anderson (1966)
44	RbBr	0–160	78.83	4.319	23.47	3.12	Present work
45	K	0–140	31.63	3.144	48.42	5.76	Present work
			34.00	2.99			Vaidya *et al* (1971)
46	Rb	0–140	21.45	3.188	51.96	7.97	Present work
			26.6	3.23			Vaidya *et al* (1971)
47	NaF	0–140	466.74	3.942	22.26	2.76	Present work
			467.4	5.18			Vaidya and Kennedy (1971)
48	RbCl	0–120	60.79	4.815	25.48	3.00	Present work
49	As	0–100	380.60	10.52	0.010	8.80	Present work
50	Nd	0–100	324.09	4.06	0.010	7.80	Present work

equation (1). The equation of state obtained is

$$\ln[V(P, T_0)/V(0, T_0)] = -\{1/[B_T(0, T_0)Z + B'_T(0, T_0)]\} \times [\![\ln\{1 + [B'_T(0, T_0)/B_T(0, T_0)Z](1 - \exp(-ZP))\}]\!] - ZP/[B_T(0, T_0)Z + B'_T(0, T_0)] \qquad (2)$$

where T_0 is some reference temperature and $B'_T(0, T_0)$ is the first pressure derivative of the bulk modulus $B_T(0, T_0)$. Recently, this equation has been successfully applied in the case of NaCl and CsCl in the pressure range 0–400 kbar and temperature range 298–1073 K, by Kumari and Dass (1990, hereafter referred to as I).

The following points are to be noted here.

(i) As $P \to \infty$, $V(P, T_0) \to 0$.

(ii) The first part of the right-hand side of equation (2) represents the low-pressure compression whereas the second part represents the high-pressure compression.

Equation (2) has been obtained on the basis that the ratio of the second to first pressure derivative of the isothermal bulk modulus is a pressure-independent parameter, i.e.

$$[\partial^2 B_T(P, T)/\partial P^2]_T/[\partial B_T(P, T)/\partial P]_T = -Z. \tag{3}$$

Successive integration of equation (3) at the reference temperature T_0 gives rise to equation (2) along with the following equations:

$$B'_T(P, T_0) = B'_T(0, T_0)\exp(-ZP) \tag{4}$$

and

$$B_T(P, T_0) = B_T(0, T_0) + [B'_T(0, T_0)/Z][1 - \exp(-ZP)]. \tag{5}$$

Before making use of equation (2) in studying the volume compression data in solids, it will be appropriate at this juncture to justify the assumption taken in equation (3). Some justifications in this connection have already been discussed in I. However, some more points may be mentioned here which will validate the assumption.

(i) The calculations for $V(P, T_0)/V(0, T_0)$ in the pressure range 0–4500 kbar agree very well with the experimental data for copper as the root mean square deviation (RMSD) obtained is 5.2×10^{-4} (see table 1). Hence, these calculations clearly give confidence in the correctness of the assumption.

(ii) The present equation of state has been applied in case of n-H_2 and n-D_2 to 25 kbar at 4.2 K. The values of $V(P, T_0)/V(0, T_0)$ and $B_T(P, T_0)$ obtained by us are found to be in very good agreement with the values reported by Anderson and Swenson (1974). Very good agreement for these properties in both the solids suggests the correctness of the assumption. These results are to be published later.

(iii) In the literature, we find the following relation given by Grover *et al* (1973):

$$B_T(P, T) = B_T(0, T)\exp[\alpha(\Delta V/V(0, T))]$$

where $\Delta V = V(0, T) - V(P, T)$ and α is a constant which has been identified as $B'_T(0, T)$ (Kumari and Dass, 1987). This relation gives

$$[\partial^2 B_T(P, T)/\partial P^2]_T/[\partial B_T(P, T)/\partial P]_T = -1/B_T(P, T).$$

We believe that our assumption gives a better fit to the experimental data than that of Grover *et al* (1973).

Therefore, taking all these points into consideration along with the points discussed in I, we feel that the present assumption given in equation (3) is a good working assumption.

Hence equation (2) has been applied to the volume compression data of 50 solids. The values of the adjustable parameters $B_T(0, T_0)$, $B'_T(0, T_0)$ and Z obtained by fitting the compression data are reported in table 1 along with firstly the pressure range used in the present study and secondly the RMSD of $V(P, T_0)/V(0, T_0)$. Further, the values of $B_T(0, T_0)$ and $B'_T(0, T_0)$ available from other workers are also reported in table 1 for comparison.

The following points are worth noting from table 1.

(i) The maximum pressure range and minimum pressure range used in the present study are 0–4500 kbar and 0–100 kbar, respectively.

(ii) In almost all cases, the present calculated values of $B_T(0, T_0)$ are in good agreement with the values given by other workers. However, there are a few exceptions.

(iii) The value of the RMSD obtained for $V(P, T_0)/V(0, T_0)$ in the present calculation for all the solids clearly suggests the success and the usefulness of the present equation of state.

(iv) Equations (5) and (4) can be used to calculate the pressure dependence of bulk modulus and its first pressure derivative, i.e. the values of $B_T(P, T_0)$ and $B'_T(P, T_0)$. The calculations for these parameters are not reported to save space.

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