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On the tests of universality for isothermal equations of state

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Abstract. The universality of both the Birch equation and the equation of Vinet *et al* is tested and discussed using the compressibility data for the 15 transition metals and 22 compounds.

The isothermal equation of state of a solid at a given temperature can be used to describe the relation between the pressure P and the compression V/V_0 (V_0 is the zero-pressure volume) of a solid at high pressures. There are three widely used isothermal equations of state. They are the Murnaghan equation, the Birch equation and the equation of Vinet *et al*.

Murnaghan [1] assumed that the bulk modulus B is linear with the pressure P, i.e.

$$B = B_0 + B_0' P.$$

From the definition of the bulk modulus $B = -V(\partial P/\partial V)_T$, the following equation of state is immediately derived:

$$P = (B_0/B_0')(x^{-3B_0'} - 1) \tag{1}$$

where $x = (V/V_0)^{1/3}$; B_0 and B_0' are the bulk modulus and its first pressure derivative at zero pressure, respectively. Usually equation (1) is called the Murnaghan equation. The experimental results show that the Murnaghan equation only holds good until $(V/V_0)_{\min} \simeq 0.8$ [2]. If the compression V/V_0 is continuously decreased with increasing pressure, then the discrepancies between equation (1) and the experimental results become more and more serious. Therefore, equation (1) is not considered in this work.

The second equation of state is the Birch [3] equation

$$P = \tfrac{3}{2}B_0 x^{-5} \sum_{i=1} b_i (x^{-2} - 1)^i \tag{2}$$

where the first two expansion coefficients are $b_1 = 1$ and $b_2 = \tfrac{3}{4}(B_0' - 4)$. If only the first two terms in equation (2) are considered, then equation (2) can be written as

$$P = \tfrac{3}{2}B_0(x^{-7} - x^{-5})[1 + \tfrac{3}{4}(B_0' - 4)(x^{-2} - 1)]. \tag{3}$$

Of course, the Birch equation has the advantage over the Murnaghan equation. Some reports [2, 4] have shown that equation (3) applies to various classes of solid until $(V/V_0)_{\min} \simeq 0.6$.

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Table 1. The bulk modulus and its pressure derivative for 15 transition metals.

Metal	B_{0V} (GPa)	B_{0B} (GPa)	B_{0e} [8] (GPa)	B'_{0V}	B'_{0B}	B'_{0e} [9]	γ_V	γ_B	$(V/V_0)_{min}$
Ti	100.1	101.1	105.1	3.79	3.63	4.37	0.9996	−0.9945	0.625
Cr	187.3	188.8	190.1	5.81	5.56	4.89	0.9988	0.9934	0.733
Co	194.1	196.4	191.4	5.01	4.70	4.26	0.9984	0.9813	0.704
Ni	183.5	185.2	186.0	5.75	5.47	5.26	0.9986	0.9920	0.721
Cu	130.1	131.1	137.0	6.33	6.12	5.48	0.9987	0.9944	0.690
Ta	179.0	179.7	200.0	4.30	4.16	3.79	0.9997	0.8754	0.8284
W	302.4	305.0	323.2	4.57	4.34	4.33	0.9991	0.9666	0.725
Pt	278.6	279.1	278.3	5.77	5.66	5.18	0.9996	0.9971	0.8819
Au	170.5	170.5	173.2	6.67	6.61	6.29	0.9976	0.9897	0.696
Zr	92.7	91.7	83.3	2.75	2.95	4.11	0.9991	−0.9965	0.7104
Nb	165.6	166.2	170.2	4.33	4.17	4.06	0.9998	0.9265	0.8197
Mo	265.7	267.7	272.5	4.45	4.22	4.50	0.9995	0.9739	0.726
Rh	285.6	286.2	270.4	5.25	5.12	4.50	0.9999	0.9976	0.8812
Pd	166.4	165.2	180.8	7.84	8.14	5.42	0.9984	0.9934	0.8513
Ag	99.8	98.5	100.7	7.12	6.12	6.12	0.9971	0.9881	0.670

Table 2. The bulk modulus and its pressure derivative for 22 compounds.

Compound	B_{0V} (GPa)	B_{0B} (GPa)	B'_{0V}	B'_{0B}	γ_V	γ_B	$(V/V_0)_{min}$
CsCl	16.60	16.59	5.71	5.77	0.9848	0.9065	0.767
AgCl	41.64	41.64	6.93	6.93	0.9996	0.9971	0.9162
NH_4Cl	17.22	17.36	6.45	6.27	0.9957	0.9769	0.773
NaBr	19.14	19.21	5.64	5.45	0.9909	0.9320	0.778
CsBr	15.14	15.20	5.46	5.29	0.9964	0.9686	0.8252
TlBr	19.49	19.59	5.45	5.24	0.9950	0.9545	0.777
NH_4Br	16.58	16.68	5.36	5.12	0.9924	0.9252	0.756
NaI	14.55	14.71	5.16	4.87	0.9992	0.9913	0.734
RbI	1.882	1.313	9.99	18.4	0.9863	0.9837	0.602
CsI	12.18	12,34	4.93	4.61	0.9981	0.9682	0.706
TlI	15.00	14.87	7.71	8.04	0.9901	0.9650	0.8446
$RbNO_3$	18.73	18.73	5.67	5.54	0.9655	0.7837	0.781
$AgNO_3$	18.27	18.14	7.21	7.38	0.9944	0.9742	0.794
$CsNO_3$	17.62	17.62	5.56	5.43	0.9535	0.7177	0.774
BaS	33.34	30.27	10.8	11.9	0.9988	0.9953	0.9139
ZnS	75.76	74.28	12.6	14.4	0.9861	0.9791	0.924
CaSe	47.19	47.07	9.20	9.52	0.9967	0.9925	0.9282
SrSe	41.41	41.24	9.93	10.4	0.9937	0.9883	0.9225
CaTe	42.25	42.11	9.54	9.95	0.9925	0.9833	0.9227
PbTe	35.69	35.77	5.75	5.63	0.9431	0.6926	0.9002
NaCl	24.30	24.35	4.52	4.40	0.9955	0.7499	0.8840
TiCl	22.12	22.21	4.98	4.81	0.9829	0.7793	0.787

Another well known equation is the equation of Vinet *et al* [4–6]

$$P = 3B_0(1-x)x^{-2}\exp[\tfrac{3}{2}(B'_0-1)(1-x)]. \tag{4}$$

Many experimental data have shown that equation (4) is acceptably universal, i.e., even

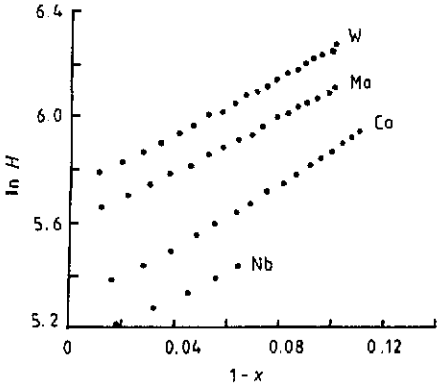

Figure 1. ln H against $1-x$ for some transition metals (W, Mo, Co and Nb).

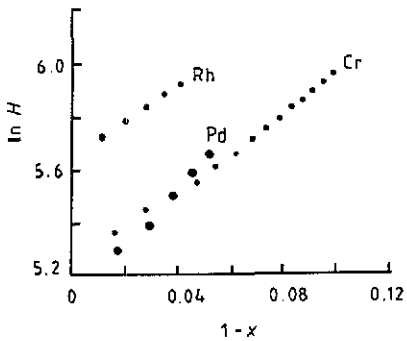

Figure 2. ln H against $1-x$ for some transition metals (Rh, Cr and Pd).

if $(V/V_0)_{min} < 0.6$, equation (4) still holds good provided that phase transitions do not occur. Vinet *et al* pointed out that equation (4) has been shown to be accurate for H_2 and D_2 up to $(V/V_0)_{min} = 0.2$.

In order to test the universality of both the Birch equation and the equation of Vinet *et al*, equations (3) and (4) have been rewritten as

$$Z = 2P/3(x^{-7} - x^{-5}) = B_0 + \tfrac{3}{4}B_0(B_0' - 4)(x^{-2} - 1) \tag{5}$$

and

$$\ln H = \ln[Px^2/3(1-x)] = \ln B_0 + \tfrac{3}{2}(B_0' - 1)(1-x). \tag{6}$$

From equations (5) and (6) we can see that the relations between Z and $x^{-2}-1$, as well as between $\ln H$ and $1-x$ are linear. Therefore, using the experimental data on compressibility of solids at high pressures we can obtain the values of the fitting parameters B_0 and B_0' in terms of the linear regression, and we can test the universality of these two equations.

Now let us test their universality using the compressibility data for 15 transition metals and 22 compounds at high pressures. The data are taken from [7]. The B_0- and B_0'-values obtained from the fitting, as well as the regression coefficient γ are listed in tables 1 and 2. In order to distinguish between the two forms of equation, the subscripts B and V represent the results of fitting the Birch equation and the equation of Vinet *et al*; the subscript e indicates the experimental value. $(V/V_0)_{min}$ is the minimum value of compression.

(1) For the 15 transition metals the agreement between B_{0B} and B_{0V} is good, and both B_{0B} and B_{0V} are in agreement with the experimental values B_{0e}. The calculated results also show that the mean relative errors between both and B_{0e} are about 4%. We can see clearly that the Birch equation and the equation of Vinet *et al* can be used to describe the isothermal compressible law of the transition metals until $(V/V_0)_{min} \simeq 0.625$.

(2) For the 15 transition metals, as far as the linear regression coefficients are concerned, there is marked agreement with equations (5) and (6), but the equation of Vinet *et al* is slightly better than the Birch equation. We shall plot $\ln H$ against $1-x$ using the compressibility data for 15 transition metals, as shown in figures 1–4. It is found

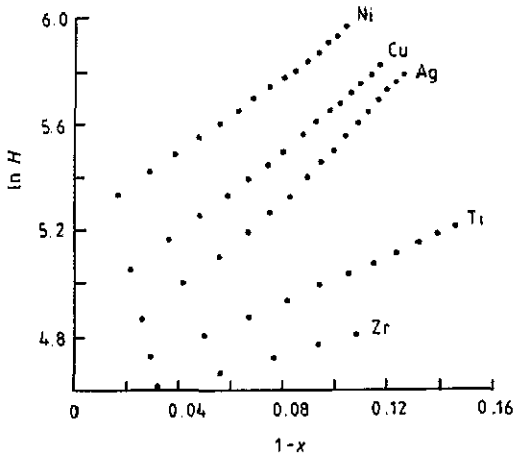

Figure 3. ln H against $1 - x$ for some transition metals (Ni, Cu, Ag, Ti and Zr).

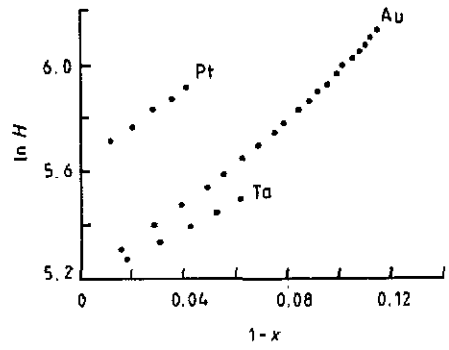

Figure 4. ln H against $1 - x$ for some transition metals (Pt, Au and Ta).

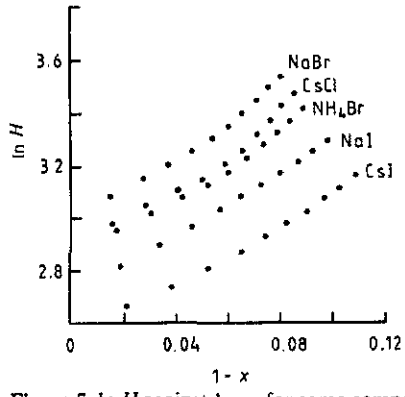

Figure 5. ln H against $1 - x$ for some compounds (NaBr, CsCl, NH_4Br, NaI and CsI).

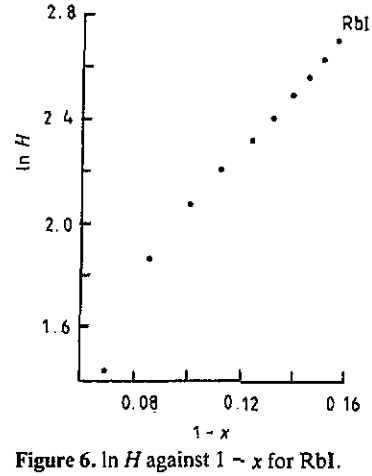

Figure 6. ln H against $1 - x$ for RbI.

that in each case the ln H plots are fitted to a straight line, except for Au when $1 - x > 0.09$ there is a slight upward curvature as x decreases.

(3) The results of the fitting show that the agreement between B_{0B} and B_{0V} is also good for 22 compounds. From table 2 we can see that, as far as the linear regression coefficients are concerned, the equation of Vinet *et al* is better than the Birch equation. Figures 5–9 show the results of plotting ln H against $1 - x$ for 11 compounds. We found that for four compounds (e.g. $AgNO_3$, $RbNO_3$, $CsNO_3$ and CsCl) the plots show non-linearity, although the values of the regression coefficient indicate a good linear fit. This non-linearity is quite clear, especially when $1 - x > 0.05$. The shape of plot is analogous to a quadratic curve. The plots of the remaining seven compounds can be clearly fitted by a straight line. This indicates that the universality of the equation of Vinet *et al* is restricted. This question needs the further study and will be discussed in another paper.

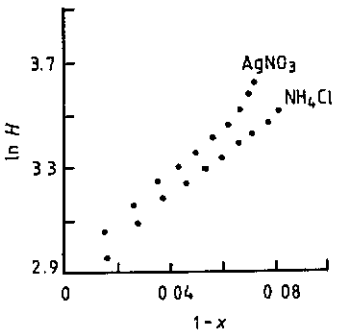

Figure 7. ln H against $1-x$ for $AgNO_3$ and NH_4Cl.

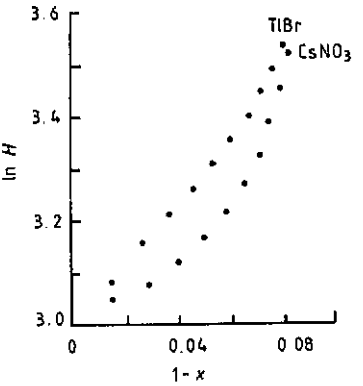

Figure 8. ln H against $1-x$ for TlBr and $CsNO_3$.

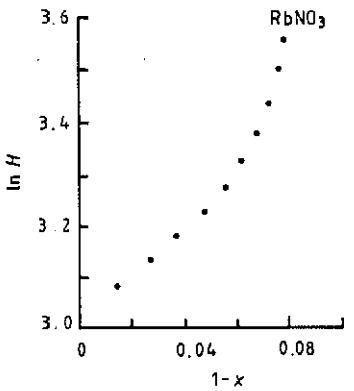

Figure 9. ln H against $1-x$ for $RbNO_3$.

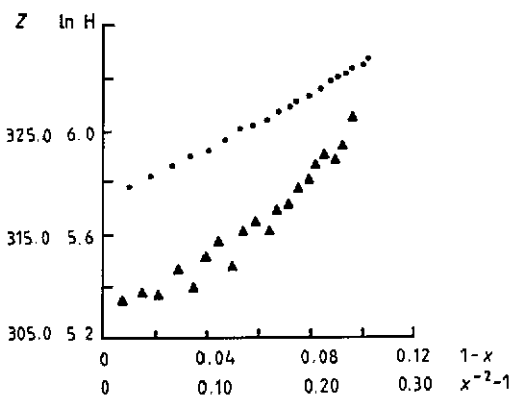

Figure 10. ln H against $(1-x)$ and Z against $x^{-2}-1$ for the transition metal W.

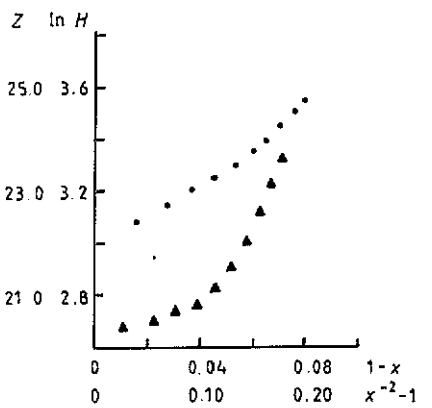

Figure 11. ln H against $(1-x)$ and Z against $x^{-2}-1$ for the compound NaBr.

(4) In order to compare equation (5) with equation (6), we shall plot Z against $x^{-2} - 1$ using the compressibility data for some materials (e.g. W and NaBr), together with ln H against $1 - x$, as shown in figure 10 (for W) and figure 11 (for NaBr). From figures 10 and 11 we can see directly that, as far as linear fit is concerned, the equation of Vinet *et al* is better than the Birch equation. In addition, if $B_0' < 4$ in equation (5), then the linear regression coefficient γ becomes negative. For example, for the transition metals Ti and Zr in table 1 their values of γ_B are negative.

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