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Failure of the Identity That Links Thermal Expansion and Isothermal Compressibility in the Case of Condensed Phases

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Author's contribution

The sole author designed, analyzed, interpreted and prepared the manuscript.

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Short Research Article

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ABSTRACT

In thermodynamics, there is a relation that connects the thermal expansion coefficient and the isothermal compressibility. It has been supposed that it was a universal identity. However, it is shown here that this identity is not appropriate for condensed phases. Experimental measurements confirm this conclusion. This relation is used in the derivation of Mayer's relation and the heat capacity ratio, and proceeds to produce results that significantly deviate from experimental results for condensed phases. An additional mistake is also detected in the derivation of Mayer's relation.

Keywords: Isothermal compressibility; adiabatic compressibility; isobaric heat capacity; isochoric heat capacity; Mayer's relation; ice 7.

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1. INTRODUCTION

There is a relationship in thermodynamics [1]:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = \beta\left(\frac{\partial P}{\partial T}\right)_V, \quad (1)$$

where α is the thermal expansion coefficient, V is the volume, T is the temperature, P is the pressure, and β is the isothermal compressibility. It has been supposed that this is a universal identity. However, one can show that it often fails for condensed phases. The third Maxwell relation is:

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad (2)$$

where S is the entropy. It can be demonstrated that $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial S}{\partial V}\right)_U + \frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T$. In most cases, when the internal energy U varies, then T varies and vice versa; hence in these cases U is constant when T is constant, and:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial S}{\partial V}\right)_U. \quad (3)$$

From Eqs. (1), (2), (3), and the combination of the first and second laws of thermodynamics:

$$\delta Q \le T\mathrm{d}S = \mathrm{d}U + P\mathrm{d}V, \quad (4)$$

it follows that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial S}{\partial V}\right)_U = \frac{\alpha}{\beta} = \frac{P}{T}. \quad (5)$$

Let us check this equation. For Fe at room temperature and atmospheric pressure, $\alpha = 3.6\times10^{-5}\ \mathrm{K}^{-1}$ [2] and $\beta = 0.594\times10^{-11}\ \mathrm{m}^2/\mathrm{N}$ [3]. Hence $\alpha/\beta = 6\times10^6\ \mathrm{m}^2/(\mathrm{N{\cdot}K})$, but $P/T = 336\ \mathrm{m}^2/(\mathrm{N{\cdot}K})$. For NaCl under the same conditions, $\alpha = 1.2\times10^{-4}\ \mathrm{K}^{-1}$ [4], $\beta = 0.42\times10^{-10}\ \mathrm{m}^2/\mathrm{N}$ [3], and $\alpha/\beta = 2.9\times10^6\ \mathrm{m}^2/(\mathrm{N{\cdot}K})$. It is clear that P in Eq. (4) is not the atmospheric pressure, but is the sum of atmospheric pressure and the pressure due to surface tension, with the former being negligibly small compared to the latter. The latter pressure is not independent of temperature. It is evident that Eq. (1) does not describe the processes in this case precisely. One can show that it is often not an identity for condensed phases. As this equation is used in the derivation of Mayer's relation and the heat capacity ratio, they also produce the wrong results for condensed phases.

2. THEORY

Let us perform a process of heat exchange, we introduce a quantity of heat into a solid or liquid (Eq. (4)). Its temperature, volume and surface tension pressure will all increase. Therefore, the volume is a function of temperature, and the temperature is a function of pressure: $V = V(T(P))$. The process is described as:

$$\mathrm{d}V = \frac{\mathrm{d}V}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}P}\mathrm{d}P. \quad (6)$$

From Eq. (6), one obtains the following equation:

$$\alpha = \frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}T} = \frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}P}\frac{\mathrm{d}P}{\mathrm{d}T} = \beta'\frac{\mathrm{d}P}{\mathrm{d}T} \quad (7)$$

The thermal expansion coefficient here is the same as that in Eq. (1). The one in Eq. (1) is measured under a constant atmospheric pressure; however, the overall pressure in the system is not constant. The compressibility β' in Eq. (7) is not at a constant temperature and is not the coefficient of compression but that of expansivity, which differs noticeably from that of compression. One can see that Eq. (1) cannot describe the process because it is derived for a function of two independent arguments: $V(T,P)$. It is instructional to present the derivation of Eq. (1). This equation follows from the triple product rule for three variables such that each variable is an implicit function of the other two [5,6]:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1. \quad (8)$$

Let us perform a simplified derivation of it. Suppose that there is a function $f(x, y, z) = 0$ (in thermodynamics, three variables can frequently be related by a function of such a form). The total differential of z is

$$\mathrm{d}z = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y \,. \quad (9)$$

Consider a curve with dz = 0 that is parameterised by x. On this curve

$$\mathrm{d}y = \left(\frac{\partial y}{\partial x}\right)_z \mathrm{d}x \,. \quad (10)$$

Therefore, the equation for dz = 0 becomes

$$0 = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \mathrm{d}x \,. \quad (11)$$

This is true for all dx; hence rearranging terms gives

$$\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \,. \quad (12)$$

Dividing this equation by its right-hand side gives the triple product rule, Eq. (8).

In the present paper, Eq. (1) has been experimentally checked for a number of solid substances and liquid gallium. In Table 1, the physical values of these substances are presented, and in Table 2, the bulk moduli ratios and heat capacity ratios are presented. The bulk modulus is the inverse of the compressibility. Here the isothermal bulk modulus, B, and the isentropic one, B_S, are considered.

Mayer's relation is:

$$C_P - C_V = \frac{T\alpha^2}{\rho\beta} \,, \quad (13)$$

where C_P and C_V are the isobaric and isochoric heat capacities respectively, and ρ is the density. The heat capacity ratio is:

$$\frac{C_P}{C_V} = \frac{\beta}{\beta_S} = \frac{B_S}{B} \quad (14)$$

where β_S is the isentropic compressibility. Equations (13) and (14) are derived using Eq. (1) without simplification, and therefore the heat capacity ratios in both equations must be equal. However, from Table 2 one can see that they differ greatly.

The authors of [7,8] report another value of B for MgO, but it is wrong because, at small deformations, solids obey Hooke's law with very high accuracy [3,4]; nonetheless, the authors use a third-order Birch-Murnaghan equation of state (which takes into account all points in the broad interval of pressures and deformations) in this linear region. For example, in [9] the deformation of MgO obeys Hooke's law up to 1.92 GPa (Fig. 1). The dependence of the volume on pressure can be given by the following equation:

$$V = 11.26 - 0.083434P \quad (15)$$

where the volume is in cubic centimetres per mole and the pressure is in gigapascals. From Eq. (15), the isothermal bulk modulus at standard

Table 1. Physical values of some solids and a liquid at room temperature

Substance	ρ, kg/m^3	α, 10^{-5} K^{-1}	C_P, J/(kgK)
Magnesiowüstite MgO	3566 (5) [7]	3.12 [7]	924 [2]
Zr	6510.7 [2]	2.0 [13]	277.3 [2]
Ga (liquid)	6094.8 [2]	5.5 [2]	373.9 [2]
Fluorite CaF_2	3181.5 (7) [10]	5.7 (7) [10]	878.5[a)] [10]
Diopside $MgCaSi_2O_6$	3286 (5) [11]	1.88 [11]	384.7 [11]
Forsterite Mg_2SiO_4	3233 [12]	2.2599 [14]	844.3 [14]

The standard deviation in the last digit is shown in parentheses. a) In [10], an erroneous value was reported: 87.85

Table 2. Bulk moduli of substances from Table 1 and their ratios

Substance	B, GPa	B_S, GPa	B_S/B	C_P/C_V, Eq. (13)
Magnesiowüstite	135.0 (10)	163.5 (11) [8]	1.21	1.012
MgO	Eq. (15)	167.1 (4)[a)] [8]		
Zr	75.1 (32) [13]	95.3 [19]	1.27	1.005
Ga	23.6 (0.5) [15]	50 (3) [15]	2.12	1.009
liquid	12.1 (6) [16]	50.4 (4) [20]	4.17	
Fluorite CaF_2	74.6 (65) [10]	84.5 (5) [10]	1.13	1.027
Diopside $MgCaSi_2O_6$	88.3 (3) [17]	116.5 (9) [11]	1.32	1.007
Forsterite	63.6 [12]	128.32 [14]	2.02	1.004
Mg_2SiO_4	80.9 [18]	128.8 (5) [21]	1.59	

For all substances except Ga, the isothermal bulk modulus was obtained in this work using the dependence of V on P in the cited literature. In [12] there are misprints: V/V_0 for P = 0.7 GPa should be 0.989, and for P = 1.3 GPa it should be 0.986. The data for 0.7 and 1.3 GPa have been interchanged. The standard deviation in the last digit is shown in parentheses. a) Calculated from the speeds of sound at ambient pressure

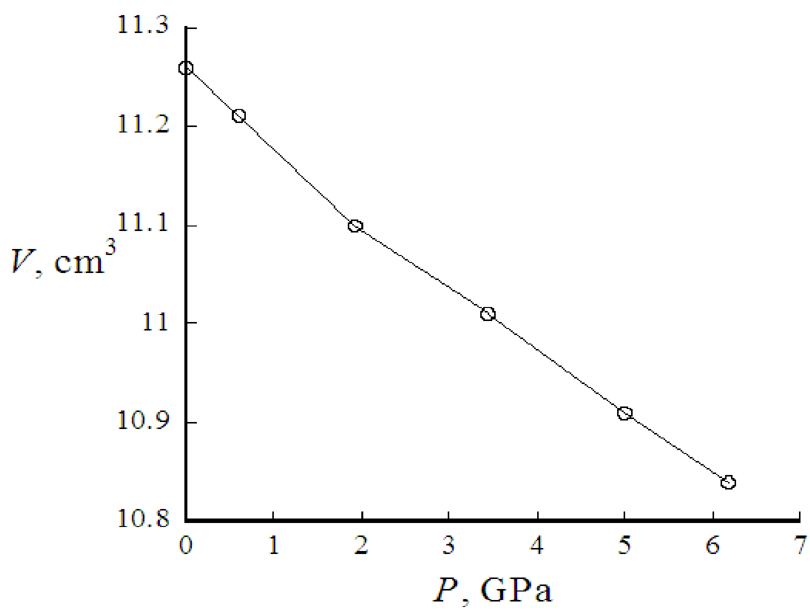

Fig. 1. Dependence of the volume on pressure for MgO [8]

ambient temperature and pressure is equal to 135.0 ± 1.0 GPa. In this paper, the bulk modulus for all substances was calculated from the data that obeyed Hooke's law.

In [22], physical properties of ice VII were measured (Table 3). Its volume depends on the pressure at room temperature according to the expression:

$$V = 7.564 + 2.743\times10^{-2}P - 9.557\times10^{-4}P^2,\quad P \le 42.0 \text{ GPa}$$

$$V \approx 7.792 - 2.47\times10^{-2}P,\quad P \ge 58.4 \text{ GPa} \quad (16)$$

It is evident that the ratio B_S/B is significantly larger than the ratio C_P/C_V obtained from Eq. (13), particularly at higher pressures. It increases up to 2 at 42 GPa and then decreases drastically.

Table 3. Compressibilities of ice VII and their ratios at room temperature

Pressure, GPa [20]	*B*, GPa, Eq. (16)	B_S, GPa [22]	B_S/B	C_P/C_V, Eq. (13)
34.4 (4)	192 (17)	233 (2)	1.21	1.00
37.3 (1)	165 (24)	237 (3)	1.44	1.00
38.7 (9)	155 (12)	245 (3)	1.58	1.00
40.3 (5)	143 (9)	260 (3)	1.82	1.00
42.0 (5)	133 (4)	261 (3)	1.96	1.00
58.4 (9)	315 (21)	383 (3)	1.22	1.00
59.7 (14)	315 (21)	395 (3)	1.25	1.00
61.8 (14)	315 (21)	417 (3)	1.32	1.00

The standard deviation in the last digit is shown in parentheses.

3. DISCUSSION AND CONCLUSIONS

One can see that the identity Eq. (1), Mayer's relation (Eq. (13)), and the heat capacity ratio (Eq. (14)) cannot describe condensed matter correctly. The derivations of these relations can be found in [23]. In the derivation of Mayer's relation and the heat capacity ratio, Eq. (1) is used. Moreover, one can show that the derivation of Mayer's relation is not correct. Let us consider the key part of this derivation and expand *S* as a function of *T* and *V*:

$$\mathrm{d}S(T,V)=\left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T+\left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V \quad (17)$$

Whence

$$\left(\frac{\partial S}{\partial T}\right)_P=\left(\frac{\partial S}{\partial T}\right)_V+\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P \quad (18)$$

and

$$C_P-C_V=T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P. \quad (19)$$

One can see that this consideration is equivalent to the following one. Let us take the following expansion:

$$\mathrm{d}S(T,V,P=\mathrm{const})=\left(\frac{\partial S}{\partial T}\right)_{V,P}\mathrm{d}T+\left(\frac{\partial S}{\partial V}\right)_{T,P}\mathrm{d}V \quad (20)$$

and divide it by d*T*. The derivatives on the right-hand side are equal to zero, and at a constant *P* the arguments *V* and *T* are not independent. Equation (1) is valid only in the ideal case where in *V*(*T*,*P*), temperature and pressure are independent parameters.

It is interesting to note that Eq. (1) was experimentally checked for rubber and the authors reported a value of –0.88 for the right-hand side of Eq. (8) [24]. Nevertheless, even this value is not reliable. In [24,25] and references therein, the tension of a rubber band, *F*, as a function of temperature and length, *L*, was measured. The authors of [24] check the following equation:

$$\left(\frac{\partial F}{\partial L}\right)_T\left(\frac{\partial L}{\partial T}\right)_F\left(\frac{\partial T}{\partial F}\right)_L=-1. \quad (21)$$

The authors measure $(\partial F/\partial T)_L>0$, where *F* is the tension of a rubber band, and assume that it equals $\left[(\partial T/\partial F)_L\right]^{-1}$, which means that both derivatives have the same sign. This is not true. It should be noted that the sign of $(\partial F/\partial L)_T$ differs from that of $(\partial L/\partial F)_T$. The former is the dependence of the tension on the length of expansion measured experimentally (the greater the expansion ΔL the greater the tension ΔF, and $\Delta F/\Delta L > 0$.) The latter is obtained only theoretically, which we demonstrate as follows. Let us increase the force of attraction between the atoms ($\Delta F > 0$), and hence the rubber will contract ($\Delta L < 0$). The sign of $(\partial L/\partial T)_F$ is negative because the rubber band contracts when heated under tension (the Gough–Joule effect) [24,25]. The derivative $(\partial T/\partial F)_L$ will be negative. Let us increase the tension by increasing the force of attraction between the atoms. As a result, the rubber band will contract. To keep the band length constant, we have to decrease its temperature according to the Gough–Joule effect. Consequently, the experiment produces the value +0.88 instead of −1. The signs of the partial derivatives of Eq. (1) obtained in [24] have been confirmed by many other papers [25]. One can see that Eqs. (1) and (8) are not reliable in the description of condensed phases.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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