Short Research Article

Identity that Connects Thermal Expansion and Isothermal Compressibility is Not an Identity for Condensed Phases

.

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. It is shown that it is often not an identity for condensed phases. Experimental measurements confirm this conclusion. This relation is used in the derivation of Mayer's relation and the heat capacity ratio; therefore Mayer's relation and the heat capacity ratio also produce the wrong results for condensed phases, which is confirmed experimentally. Another mistake in the derivation of Mayer's relation is found.

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

1. INTRODUCTION

There is a relationship in thermodynamics [1]:

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

where α is the thermal expansion coefficient, *V* is volume, *T* is temperature, *P* is 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:

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

where *S* is entropy. Often when the internal energy *U* varies, then *T* varies and vice versa. 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 cases when *T* is constant *U* is also constant; hence in these cases:

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

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

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

it follows that

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

Let us check this equation. For Fe at room temperature and atmospheric pressure, $\alpha = 3.6\times10^{-5}$ K^{-1} [2] and $\beta = 0.594\times10^{-11}$ m^2/N [3]. Hence α/β equals 6×10^6 m^2/(N·K), but P/T equals 336 m^2/(N·K). For NaCl under the same conditions, $\alpha = 1.2\times10^{-4}$ K^{-1} [4], $\beta = 0.42\times10^{-10}$ m^2/ N [3] and α/β equals 2.9×10^6 m^2/(N·K). It is clear that P in Eq. (4) is not atmospheric pressure but the sum of atmospheric pressure and pressure due to surface tension, with the former being negligibly small compared to the latter. This 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.

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 will increase, its volume will increase, and the surface tension pressure will increase. Therefore, the volume is a function of temperature, and temperature is a function of pressure: $V = V(T(P))$. The process will be described like this:

$$\mathrm{d}V = \frac{\mathrm{d}V}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}P}\mathrm{d}P. \tag{6}$$

From that, one can obtain the following equation:

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

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 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]:

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

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

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

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

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

Therefore, the equation for dz = 0 becomes

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

This is true for all d*x*; hence rearranging terms gives

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

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:

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

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

$$\frac{C_P}{C_V}=\frac{\beta}{\beta_S}=\frac{B_S}{B} \tag{14}$$

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.

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 [8]	277.3 [2]
Ga Liquid	6094.8 [2]	5.5 [2]	373.9 [2]
Fluorite CaF_2	3181.5 (7) [12]	5.7 (7) [12]	878.5$^{a)}$ [12]
Diopside $MgCaSi_2O_6$	3286 (5) [13]	1.88 [13]	384.7 [13]
Forsterite Mg_2SiO_4	3233 [15]	2.2599 [16]	844.3 [16]

The standard deviation in the last digit is shown in parentheses. a) In [12], 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) [9]	1.21	1.012
MgO	Eq. (15)	167.1 (4)$^{a)}$ [9]		
Zr	75.1 (32) [8]	95.3 [10]	1.27	1.005
Ga	23.6 (0.5) [11]	50 (3) [11]	2.12	1.009
Liquid	12.1 (6) [24]	50.4 (4) [25]	4.17	
Fluorite CaF_2	74.6 (65) [12]	84.5 (5) [12]	1.13	1.027
Diopside $MgCaSi_2O_6$	88.3 (3) [14]	116.5 (9) [13]	1.32	1.007
Forsterite	63.6 [15]	128.32 [16]	2.02	1.004
Mg_2SiO_4	80.9 [17]	128.8 (5) [18]	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 [15] 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.

The authors of [7,9] report another value of *B* for MgO, but it is wrong because, at small deformations, solids obey Hooke's law with very high accuracy [3,19], but 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 (figure 1). The dependence of the volume on pressure can be given by the following equation:

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

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

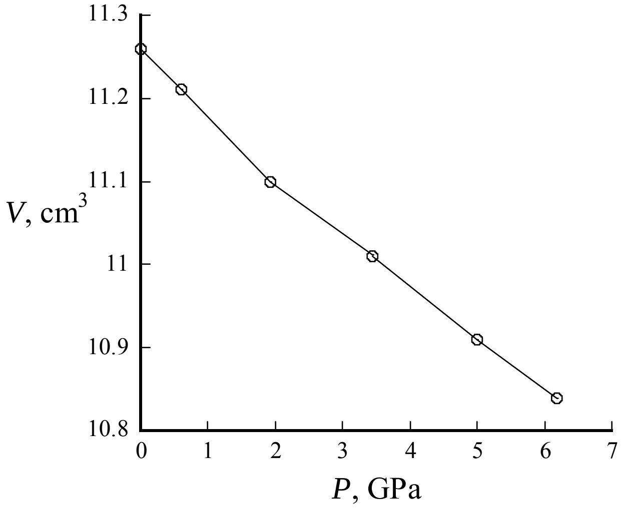

Fig. 1. Dependence of the volume on pressure for MgO [9]

In [20], physical properties of ice VII were measured (Table 3). Its volume depends on pressure at room temperature like this:

$$V = 7.564 + 2.743 \times 10^{-2} P - 9.557 \times 10^{-4} P^2, \quad P \le 42.0 \quad \text{GPa}$$

$$V \approx 7.792 - 2.47 \times 10^{-2} P, \quad P \ge 58.4 \quad \text{GPa} \qquad (16)$$

It is evident that the ratio B_S/B is significantly larger than 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 [20]**	**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, and the heat capacity ratio, Eqs. (13) and (14), cannot describe condensed matter correctly. The derivations of these relations can be found in [21]. In the derivation of Mayer’s relation and the heat capacity ratio, Eq. (1) is used. Also, 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*:

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

whence

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

and

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

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

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

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) [22]. Nevertheless, even this value is not reliable. In [22,23] and references therein, the tension of a rubber band, *F*, as a function of temperature and length, *L*, was measured. The authors of [22] check the following equation:

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

The authors measure $\left(\partial F/\partial T\right)_L>0$, where *F* is the tension of a rubber band, and assume that it equals $\left[\left(\partial T/\partial F\right)_L\right]^{-1}$, which means that both derivatives have the same sign. This is not true. It should be noted that the sign of $\left(\partial F/\partial L\right)_T$ differs from that of $\left(\partial L/\partial F\right)_T$. 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 can be obtained only theoretically: 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 $\left(\partial L/\partial T\right)_F$ is negative because the rubber band contracts when heated under tension (the Gough–Joule effect) [22,23]. The derivative $\left(\partial T/\partial F\right)_L$ 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. So, the experiment produces the value +0.88 instead of –1. The signs of the partial derivatives of Eq. (1) obtained in [22] have been confirmed by many other papers [23]. 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.

REFERENCES

1. Atkins PW. Physical chemistry. Vol 1. Oxford: Oxford University Press; 1977.

2. Chemical Encyclopaedia. Vols 1–5. Moscow: Rossijskaja Enciklopedia; 1988–1998.

3. Kittel C. Introduction to solid state physics. 8th ed. USA: John Wiley & Sons, Inc.; 2005.

4. Rao ASM, Narender K, Rao KGK, Krishna NG. Thermophysical properties of NaCl, NaBr and NaF by γ-ray attenuation technique. J Mod Phys. 2013;4(2):208–14. (Free online).
DOI: 10.4236/jmp.2013.42029

5. Elliott JR , Lira CT. Introductory chemical engineering thermodynamics. 1st ed. Prentice Hall PTR; 1999;184.

6. Carter AH. Classical and statistical thermodynamics. Prentice Hall; 2001;392.

7. Li B, Woody K, Kung J. Elasticity of MgO to 11 GPa with an independent absolute pressure scale: Implications for pressure calibration. J Geophys Res. 2006;111(11):B11206.
DOI: 10.1029/2005JB004251

8. Zhao Y, Zhang J, Pantea C, Qian J, Daemen LL, Rigg PA, et al. Thermal equations of state of the α, β, and ω phases of zirconium. Phys Rev B. 2005;71(18):184119.
DOI: 10.1103/PhysRevB.71.184119

9. Fei Y. Effects of temperature and composition on the bulk modulus of (Mg,Fe)O. Am Mineral. 1999;84(3):272–6.
DOI: 10.2138/am-1999-0308

10. Liu W, Li B, Wang L, Zhang J, Zhao Y. Simultaneous ultrasonic and synchrotron x-ray studies on pressure induced α-ω phase transition in zirconium. J Appl Phys. 2008;104(7): 076102.
DOI: 10.1063/1.2987001

11. Li R, Li L, Yu T, Wang L, Chen J, Wang Y, et al. Study of liquid gallium as a function of pressure and temperature using synchrotron x-ray microtomography and x-ray diffraction. Appl Phys Lett. 2014;105(4):041906.
DOI: 10.1063/1.4891572

12. Speziale S, Duffy TS. Single-crystal elastic constants of fluorite (CaF_2) to 9.3 GPa. Phys Chem Minerals. 2002;29(7):465–72.
DOI: 10.1007/s00269-002-0250-x

13. Isaak DG, Ohno I, Lee PC. The elastic constants of monoclinic single-crystal chrome-diopside to 1,300 K. Phys Chem Minerals. 2006;32(10):691–9.

DOI: 10.1007/s00269-005-0047-9

14. Zhang L, Ahsbahs H, Hafner SS, Kutoglu A. Single-crystal compression and crystal structure of clinopyroxene up to 10 GPa. Am Mineral. 1997;82(3–4):245–58.

15. Andrault D, Bouhifd MA, Itié JP, Richet P. Compression and amorphization of $(Mg,Fe)_2SiO_4$ olivines: An x-ray diffraction study up to 70 GPa. Phys Chem Minerals. 1995;22(2):99–107.

16. Dorogokupets PI, Dymshits AM, Sokolova TS, Danilov BS, Litasov KD. The equations of state of forsterite, wadsleyite, ringwoodite, akimotoite, $MgSiO_3$-perovskite, and postperovskite and phase diagram for the Mg_2SiO_4 system at pressures of up to 130 GPa. Russ Geol Geophys. 2015;56(1–2):172–89.
DOI: 10.1016/j.rgg.2015.01.011

17. Will G, Hoffbauer W, Hinze E, Lauterjung J. The compressibility of forsterite up to 300 kbar measured with synchrotron radiation. Physica B. 1986;139&140:193–7.
DOI: 10.1016/0378-4363(86)90556-5

18. Zha C-S, Duffy TS, Downs RT, Mao H-K, Hemley RJ. Sound velocity and elasticity of single-crystal forsterite to 16 GPa. J Geophys Res. 1996;101(B8):17535–45.
DOI: 10.1029/96JB01266

19. Auld BA. Acoustic fields and waves. Vol 1. New York: John Wiley & Sons; 1973.

20. Asahara Y, Hirose K, Ohishi Y, Hirao N, Murakami M. Thermoelastic properties of ice VII and its high-pressure polymorphs: Implications for dynamics of cold slab subduction in the lower mantle. Earth Planet Sci Lett. 2010;299(3–4):474–82.
DOI: 10.1016/j.epsl.2010.09.037

21. Adkins CJ. Equilibrium thermodynamics. 3rd ed. Cambridge: Cambridge University Press; 1983;114.

22. Carrolla HB, Eisner M, Henson RM. Rubber band experiment in thermodynamics. Am J Phys. 1963;31(10):808.
DOI: 10.1119/1.1969109

23. Roundy D, Rogers M. Exploring the thermodynamics of a rubber band. Am J Phys. 2013; 81(1):20–3.
DOI: 10.1119/1.4757908

24. Yu T, Chen J, Ehm L, Huang S, Guo Q, Luo S-N, et al. Study of liquid gallium at high pressure using synchrotron x-ray. J Appl Phys. 2012;111(11):112629.
DOI: 10.1063/1.4726256

25. Ayrinhac S, Gauthier M, Le Marchand G, Morand M, Bergame F, Decremps F. Thermodynamic properties of liquid gallium from picosecond acoustic velocity measurements. J Phys Condens Matter. 2015;27(27):275103.
DOI: 10.1088/0953-8984/27/27/275103