Journal of Thermal Analysis and Calorimetry, Vol. 95 (2009) 1, 313–317

HEAT CAPACITY INCREASES WITH PRESSURE

V. A. Drebushchak[1,2,3]*

[1]Institute of Geology and Mineralogy SB RAS, Pr. Ac. Koptyuga 3, Novosibirsk 630090, Russia
[2]Institute of Inorganic Chemistry SB RAS, Pr. Ac. Lavrentieva 3, Novosibirsk 630090, Russia
[3]Novosibirsk State University, Ul. Pirogova 2, Novosibirsk 630090, Russia

Conventional thermodynamic expression predicts that the isobaric heat capacity decreases with increasing pressure. In model calculations, heat capacity increases with pressure, decreases, or remains insensitive to pressure, depending on the model applied. The expression cannot be applied to the gases, but experimental data on gases show evidently that heat capacity increases with pressure.

Considering the change in enthalpy along two different paths with identical starting and ending points, we derive new expression $dC_P/dP=\alpha V$, where α is the volume coefficient of thermal expansion and V is the molar volume. The expression predicts the increase in C_P with pressure and can be applied to gases. The test of the new expression against accurate literature data on the heat capacity of air, gaseous and liquid, demonstrates its validity.

Keywords: *air, gases, heat capacity, pressure, thermodynamics*

Introduction

Heat capacity is a key property of a thermodynamic phase, because its entropy, enthalpy, etc., are derived from experimental data on isobaric heat capacity, $C_P(T)$. The latter is measured usually under ambient pressure and can be extrapolated up to high pressure according to thermodynamic relations or model evaluations. Thermodynamic relationship between heat capacity and pressure is

$$\left(\frac{\partial C_P}{\partial P}\right)_T=-TV\left[\alpha^2+\left(\frac{\partial\alpha}{\partial T}\right)_P\right] \quad (1)$$

where V is the molar volume, T is the temperature and α is the volume coefficient of thermal expansion [1]. Equation (1) is known for many decades. Eq. (1) in its intermediate form was used as a problem for self-testing in the monograph by Lewis and Randall, 1923 [2]. Variables and coefficients in the right-hand part of formula (1) are each positive for solids and liquids. Sign 'minus' before the whole right-hand part means that the heat capacity always decreases with increasing pressure. Sometimes this leads to spurious predictions of negative heat capacity at high pressures [3].

Experimental data on heat capacity of condensed matter under high pressure are scarce and inaccurate, because direct and accurate adiabatic calorimetry developed for ambient pressure can be hardly adapted to the devices generating high pressure [4–6]. Indirect measurements are based, for example, on the transient hot-wire techniques, measuring a product of 'heat capacity·heat conductivity' [7]. Coefficient of heat conductivity under ambient pressure is known with much less accuracy (~5%) than heat capacity (~0.5%). The increase of C_P for amorphous SiO_2 by 0.1% when P increases by 1 GPa is considered in good agreement with the decrease of 0.0%, calculated after Eq. (1) [8].

The lack of experimental data is filled with the model relationships, allowing one to derive heat capacity from the equation of state (EOS), interatomic potential, molecular dynamics, etc. Heat capacity increases with pressure, decreases, or remains almost insensitive to pressure, depending on the model applied. It is difficult to recognize a general tendency in the changes of 'model' C_P with pressure. Heat capacity decreases with pressure for liquid SiO_2 [9] and increases for liquid MgO [10]. It is reasonable that pressure increases frequency of atomic vibration in solids, increasing Debye temperature and, hence, decreasing heat capacity if the latter is less than the Dulong–Petit value ($3R$ per atom) [11, 12]. The same is valid for organic solids and liquids, where C_P decreases with pressure [13]. Nevertheless, room-temperature heat capacity of MgO increases from 30.04 J mol^{-1} K^{-1} at 0.1 MPa to 31.71 J mol^{-1} K^{-1} at 35 GPa [14]. Heat capacity of iron decreases with pressure at low temperatures and increases at high temperatures due to the increase in electronic heat capacity with pressure [15], but, according to another model, electronic heat capacity in iron decreases with pressure [16].

Measurements of heat capacity of gases under pressure are much accurate than those for solids and liquids. Gases do not possess electronic heat capacity

---

* Author for correspondence: dva@uiggm.nsc.ru, dva@xray.nsu.ru

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

or Debye temperature. They are most suitable for the testing of thermodynamic relation between C_P and pressure. Unfortunately, sixty years ago experiments showed that Eq. (1) is poorly applicable to gases [17]. The differentiations of the P–V–T values were found to be so sensitive to the analytic methods of handling the data that the direct experimental determination is to be preferred [18]. In applying Eq. (1) to the ideal gas, we see that pressure does not affect its heat capacity:

$$\alpha = \frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}T};\ V = \frac{RT}{P} \Rightarrow \alpha = \frac{1}{T} \qquad (2)$$

Substituting

$$\alpha^2 = \frac{1}{T^2} \text{ and } \left(\frac{\partial\alpha}{\partial T}\right)_P = -\frac{1}{T^2} \text{in (1), we receive}$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = 0$$

Experimental data certainly prove that the heat capacity of gases increases with pressure. The less temperature, the greater the increase [17]. Why does Eq. (1) describe gases incorrectly?

Equation (1) is derived from another equations by the differentiation:

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P;\ \left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^3 G}{\partial P\partial T^2}\right)$$

Then the order of the differentiation is changed

$$\frac{\partial^3 G}{\partial P\partial T^2} = \frac{\partial^3 G}{\partial T^2\partial P} \text{ and } \left(\frac{\partial G}{\partial P}\right)_T = V$$

Equation (1) is useless for ideal gases because

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_P \equiv 0 \text{ for } V = \frac{RT}{P}$$

Substitution of the derivatives for the thermal expansion coefficient does not change the fact that the right-hand part of Eq. (1) is equal to zero.

The objective of the work was to derive new expression for the relationship between pressure and heat capacity. Mathematical operations with thermodynamic functions are universal for all phases, solid, liquid or gaseous. The phases differ from one another in the values of their thermodynamic properties and derivatives. Experimental data on gases exhibit the greatest effect in the heat capacity as compared with solids and liquids and the new expression is to be applicable to gases, allowing us to test it most accurately.

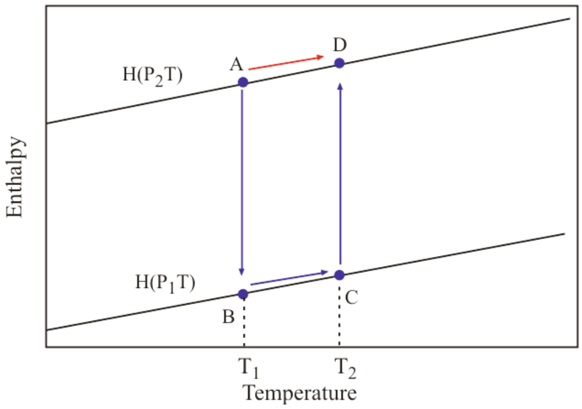

Fig. 1 Two paths for the evaluation of enthalpy change between points A (P_2,T_1) and D (P_2,T_2): one-stage A→D and three-stage A→B→C→D

Deriving new expression

The disadvantage of old expression (1) arose from the sequence of differentiations and we should use differentiation as less as possible. Enthalpy as a function of temperature is shown in Fig. 1 for two pressures, P_1 and P_2. Enthalpy increases with pressure because $\mathrm{d}H=T\mathrm{d}S+V\mathrm{d}P$ and $V\mathrm{d}P>0$. Upper line in Fig. 1 is for the greater pressure, $P_2>P_1$. Enthalpy is a potential, depending only on the starting and final variables, not on the path of the change. Two ways of the enthalpy change between points A (T_1,P_2) and D (T_2,P_2) are shown in Fig. 1: one-stage isobaric heating from T_1 to T_2 (A→D) and three-stage path with decreasing in pressure (A→B), isobaric heating (B→C) and increasing in pressure (C→D). Enthalpy changes on the stages are

$$\text{A}\rightarrow\text{D: } H(P_2, T_2)-H(P_2, T_1)$$

$$\text{A}\rightarrow\text{B: } H(P_1, T_1)-H(P_2, T_1)=\int_{P_2}^{P_1} V(T_1)\mathrm{d}P$$

$$\text{B}\rightarrow\text{C: } H(P_1, T_2)-H(P_1, T_1)$$

$$\text{C}\rightarrow\text{D: } H(P_2, T_2)-H(P_1, T_2)=\int_{P_1}^{P_2} V(T_2)\mathrm{d}P$$

The enthalpy changes on both paths are equal:

$$H(P_2, T_2)-H(P_2, T_1)=\int_{P_2}^{P_1} V(T_1)\mathrm{d}P+H(P_1, T_2)-$$

$$-H(P_1, T_1)+\int_{P_1}^{P_2} V(T_2)\mathrm{d}P=H(P_1, T_2)-H(P_1, T_1)+$$

$$\int_{P_1}^{P_2}[V(T_2)-V(T_1)]\mathrm{d}P$$

Let us change designations $T_1=T$ and $T_2=T+\Delta T$ and divide the whole expression by ΔT:

$$\frac{H(P_2T+\Delta T)-H(P_2T)}{\Delta T}=\frac{H(P_1T+\Delta T)-H(P_1T)}{\Delta T}+\int_{P_1}^{P_2}\frac{V(T+\Delta T)-V(T)}{\Delta T}\mathrm{d}P$$

The equation is valid for all values of ΔT, including infinitesimal. By definition

$$\lim_{\Delta x\to 0}\frac{f(x+\Delta x)-f(x)}{\Delta x}=\frac{\mathrm{d}f}{\mathrm{d}x}$$

for $\Delta T\to 0$ we have

$$\left(\frac{\mathrm{d}H(P_2)}{\mathrm{d}T}\right)_{\mathrm{P}}=\left(\frac{\mathrm{d}H(P_1)}{\mathrm{d}T}\right)_{\mathrm{P}}+\int_{P_1}^{P_2}\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_{\mathrm{P}}\mathrm{d}P$$

or

$$C_{\mathrm{P}}(P_2,T)=C_{\mathrm{P}}(P_1,T)+\int_{P_1}^{P_2}\alpha(T)V(T)\mathrm{d}P \tag{3}$$

Differential form equivalent to Eq. (1) is

$$\left(\frac{\mathrm{d}C_{\mathrm{P}}}{\mathrm{d}P}\right)_{\mathrm{T}}=\alpha(T)V(T) \tag{4}$$

Now right-hand part is positive and heat capacity increases with pressure. This agrees with experimental results observed for gases seventy years ago. Using Eq. (2), we can integrate Eq. (3)

$$C_{\mathrm{P}}(P_2,T)=C_{\mathrm{P}}(P_1,T)+R\ln\frac{P_2}{P_1}$$

For ideal gas $C_{\mathrm{P}}=C_{\mathrm{V}}+R$ and

$$\left(\frac{\mathrm{d}C_{\mathrm{P}}}{\mathrm{d}P}\right)_{\mathrm{T}}=\left(\frac{\mathrm{d}C_{\mathrm{V}}}{\mathrm{d}P}\right)_{\mathrm{T}}\quad C_{\mathrm{V}}(P_2,T)=C_{\mathrm{V}}(P_1,T)+R\ln\frac{P_2}{P_1} \tag{5}$$

Having V=const. and using Eq. (2) again, we derive from Eq. (4)

$$\left(\frac{\mathrm{d}C_{\mathrm{V}}}{\mathrm{d}P}\right)_{\mathrm{T}}=\frac{\mathrm{const.}}{T}$$

The less the temperature, the greater the increase in heat capacity. It explains at long last the finding of old calorimetric experiments on gases under pressure [17].

Testing new expression

To test Eq. (4) more thoroughly, we will use accurate experimental data on isochoric heat capacity of air [19]. The measurements were carried out in a calorimeter designed in the National Bureau of Standards (US). All experimental points published in [19] are shown in Fig. 2. Pressure in the calorimeter changes together with temperature during the heating and experimental points are distributed in a wide range of temperature and pressure (not shown in the figure, but listed in the table of experimental results in [19]). For 'isothermal' section, we will use the points near 150, 200 and 250 K. They are shown in the figure by large marks, with the arrows pointed at them.

Experimental data for $C_{\mathrm{V}}(P,200)$ and $C_{\mathrm{V}}(P,250)$ are shown in Fig. 3. One can see that *i*) heat capacity actually increases with pressure, *ii*) the increase is not linear, *iii*) the increase at 200 K is greater than that at 250 K.

To check logarithm relationship between heat capacity and pressure predicted by Eq. (5), we plotted

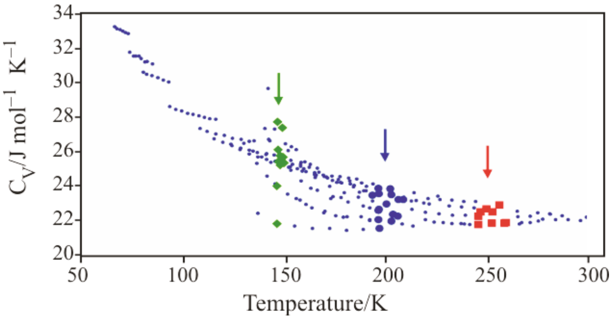

Fig. 2 Experimental points on the heat capacity of air [19]. Arrows indicate at the points for testing isothermal sections: ◆ – near 150, ● – 200 and ■ – 250 K

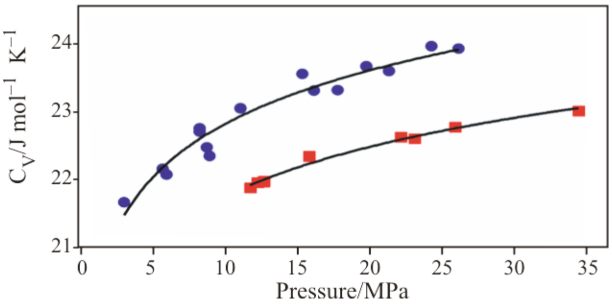

Fig. 3 Isochoric heat capacity as a function of pressure for ● – 200 and ■ – 250 K

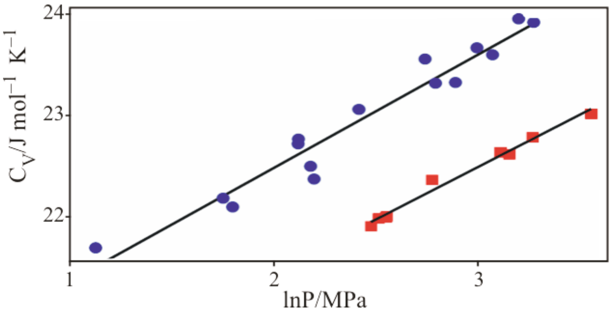

Fig. 4 Testing Eq. (5) for isochoric heat capacity for ● – 200 and ■ – 250 K

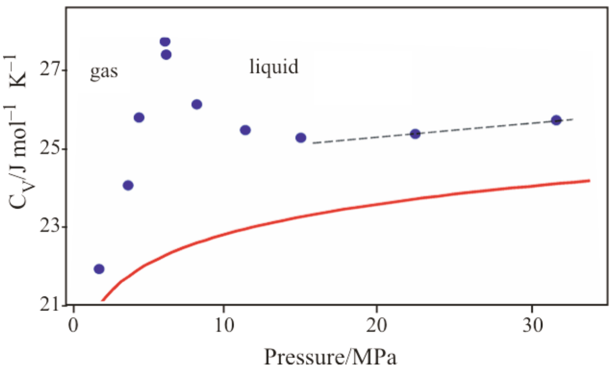

Fig. 5 Isochoric heat capacity at 150 K. Peak near 6.4 MPa is a liquefaction of air. — – Regular function $C_V(P,200)$ is shown for comparison

C_V *vs*. ln$P$ (Fig. 4). Experimental points fit well to linear regression C_V=1.154ln$P$+20.16 for 200 K and C_V=1.066ln$P$+19.28 for 250 K. Coefficient of the slope for ideal gas must be 1.000 exactly.

The main reason of the difference between the coefficients, experimental and theoretical, is in non-ideality of air. It is seen well in Fig. 5, with points in a temperature range of 145–150 K. Increase in pressure liquefies the air inside the calorimeter. It is conventional to see the peak of heat capacity near the transition point in temperature, but here we see the transition point in pressure, near 6.4 MPa. Heat capacity of such a gas differs significantly from that of ideal gas. It is interesting that the points near 150 K were measured by mistake. Magee considered air as a homogeneous gas with a critical temperature of 132.52 K [19]. Its experimental points near 150 K produced very large discrepancy with the values calculated using a literature model. Critical parameters of constituent gases are in fact 126.05 K and 3.35 MPa for nitrogen, 151.05 K and 4.8 MPa for argon and 154.35 K and 4.97 MPa for oxygen [20]. Thus, the Figure shows liquefaction of argon and oxygen at increasing pressure.

Heat capacity near 6.4 MPa consists of two contributions, (1) regular increase proportional to ln$P$ and (2) anomalous peak with a maximum at 6.4 MPa. Regular heat capacity for 200 K is shown for comparison (solid line). Anomalous contribution above 6.4 MPa decreases with increasing pressure, tending to zero. Total heat capacity decreases too, until the increase in regular contribution exceeds the decrease in anomalous contribution. Then the heat capacity starts to grow again. Two last points in Fig. 5 indicate this increase.

Points above 6.4 MPa in Fig. 5 are for liquid air. The increase in heat capacity of a liquid agrees with new expression (4) and disagrees with old one (1), because both thermal expansion coefficient and its first derivative with respect to temperature are usually positive for liquids. Nevertheless, Fig. 5 shows results too close to the critical point and properties of the liquid are close to those of a gas. It is interesting to test expression (4) with the heat capacity of 'true' liquid air, below the critical point of nitrogen. Most suitable are two points near 82 K. Heat capacity of liquid air is 31.31 J mol^{-1} K^{-1} at 82.105 K and 25.0577 MPa but 30.58 J mol^{-1} K^{-1} at 81.869 K and 11.7077 MPa. Thus, heat capacity of liquid air certainly increases with pressure.

Conclusions

New expression for the relationship between heat capacity and pressure was derived from simple thermodynamic consideration of the enthalpy change between two isobaric points. Contrary to the old expression, new one predicts that the heat capacity increases with pressure.

New expression can be applied directly to gases, unlike the old one. Accurate literature data on heat capacity of air prove its validity:

- heat capacity of gaseous air increases with pressure, proportional to the logarithm of pressure
- the effect increases with decreasing temperature
- heat capacity of liquid air also increases with pressure.

These experimental relations for gases were known for about 70 years, but without thermodynamic explanation.

Old expression predicts that the heat capacity decreases with pressure. We do not know what is the reason of the drastic discrepancy between old and new expressions. Probably, incorrect result in the old expression arose from the change in the differentiation order.

References

1 B. Wunderlich and H. Baur, Adv. Polym. Sci., 7 (1970) 151.
2 G. N. Lewis and M. Randall, Thermodynamics and the Free Energy of Chemical Substances, McGraw-Hill, New York 1923, p. 653. (German edition of 1927, Russian edition of 1936).
3 E. Brosh, G. Makov and R. Z. Shneck, CALPHAD, 31 (2007) 173.
4 M. A. Kuznetsov and S. I. Lazarev, Meas. Tech., 48 (2005) 798.
5 Y. Uwatoko, T. Fujiwara, M. Hedo, F. Tomioka and I. Umehara, J. Phys. Cond. Matt., 17 (2005) S1011.
6 P. J. van Ekeren and E. R. T. Bevers, J. Therm. Anal. Cal., 90 (2007) 931.
7 B. Hakansson, P. Andersson and G. Backstrom, Rev. Sci. Instrum., 59 (1988) 2269.

8 S. Andersson and L. Dzhavadov, J. Phys. Cond. Matt., 4 (1992) 6209.
9 B. B. Karki, D. Bhattarai and L. Stixrude, Phys. Rev. B, 76 (2007) 104205.
10 B. B. Karki, D. Bhattarai and L. Stixrude, Phys. Rev. B, 73 (2006) 174208.
11 G. P. Johari and O. Andersson, Phys. Rev. B, 73 (2006) 094202.
12 I. Hamdi, M. Aouissi, A. Qteish and N. Meskini, Phys. Rev. B, 73 (2006) 174114.
13 Y. Miyake, D. Bessières, F. Plantier, H. Ushiki and C. Boned, J. Therm. Anal. Cal., 91 (2008) 347.
14 S. Ghose, M. Krisch, A. R. Oganov, A. Beraud, A. Bosak, R. Gulve, R. Seelaboyina, H. Yang and S. K. Saxena, Phys. Rev. Lett., 96 (2006) 035507.
15 X. Sha and R. E. Cohen, Phys. Rev. B, 73 (2006) 104303.
16 D. Alfe, G. D. Price and M. J. Gillan, Phys. Rev. B, 64 (2001) 045123.
17 P. W. Bridgman, Rev. Mod. Phys., 18 (1946) 1.
18 L. G. Hoxton, Phys. Rev., 36 (1930) 1091.
19 J. W. Magee, Int. J. Thermophys., 15 (1994) 849.
20 S. Bretsznejder, Properties of Gases and Liquids. Khimija, Moscow 1966, p. 535 (in Russian, translated from Polish).

Received: May 6, 2008
Accepted: June, 13, 2008

DOI: 10.1007/s10973-008-9221-x