Short Communication

Adiabatic Lapse Rate of Water Is Negative Due to the Negative Compressibility

ABSTRACT

When the pressure of a fluid changes without the addition of heat, the temperature of the fluid changes; the rate at which the temperature changes with pressure is called the adiabatic lapse rate. According to thermodynamic equations, the adiabatic lapse rate is positive if the thermal expansion coefficient is positive, and negative if this coefficient is negative. Experiments show, however, that the adiabatic lapse rate is also positive for substances with negative thermal expansion, although for water it is negative when it has negative thermal expansion. In the present paper, a theory is developed which shows that the adiabatic lapse rate must be always positive, but is negative for water because it has negative compressibility in that temperature-pressure region. Numerous substances with negative compressibility have already been identified.

Keywords: adiabatic lapse rate; adiabatic temperature gradient; ocean thermodynamics; water; negative thermal expansion; negative compressibility; internal energy; enthalpy

1. INTRODUCTION

According to conventional theory, the adiabatic lapse rate $\left(\partial T/\partial P\right)_S$ is positive if the thermal expansion coefficient α is positive, and negative for negative α [1–4]:

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\alpha T V}{C_P} \ . \tag{1}$$

Here T is the absolute temperature, P is the pressure, S is the entropy, V is the volume, and C_P is the isobaric heat capacity. In the present paper, this phenomenon is explained for water with zero salinity. Taking the salinity into account does not change the results of the theory [1]. However, the derivative of the internal energy U, $\left(\partial U/\partial P\right)_S$, is always positive [5]:

$$\left(\frac{\partial U}{\partial P}\right)_S = \frac{\beta C_V P V}{C_P} \ , \tag{2}$$

where C_V is the isochoric heat capacity, and $\beta = -1/V\left(\partial V/\partial P\right)_T$ is the isothermal compressibility. The increase in the internal energy dU due to pressure is equal to C_SdT, where C_S is the heat capacity at constant entropy, $\left(\partial U/\partial T\right)_S$, and d$T$ is the increase in temperature due to the pressure [5]:

$$\left(\frac{\partial U}{\partial T}\right)_S = \frac{\beta C_V P}{\alpha T} \ . \tag{3}$$

Therefore, for negative α, C_S and dT must be negative. In this paper it is shown that C_S and dT must be positive regardless of the sign of α; however, if dT is negative for water, then this is due to its negative compressibility. These results are confirmed by experiment.

2. THEORY

If $C_S < 0$ at $\alpha < 0$, then by virtue of Eqs. (1)–(3), the temperature decreases when the internal energy increases. This cannot be true for a substance with positive compressibility, since if a quantity of heat δQ is introduced into water at $\alpha < 0$, both its internal energy and its temperature increase. According to Joule's principle of equivalence of heat and work, it makes no difference whether the internal energy is increased by introducing a quantity of heat or by compression.

The internal energy is the sum of the kinetic and potential energies:

$$U = K + \Pi \qquad (4)$$

In accordance with traditional theory, for substances with negative thermal expansion, when internal energy increases in Eq. (4), kinetic energy decreases and potential energy increases [1]. Under compression, the internal energy changes by dU:

$$\mathrm{d}U = \left(\frac{\partial U}{\partial K}\right)_{\Pi} \mathrm{d}K + \left(\frac{\partial U}{\partial \Pi}\right)_{K} \mathrm{d}\Pi \ . \qquad (5)$$

The first differential on the right-hand side of Eq. (5) always increases with U. This means that the temperature also increases, because the derivative is positive and equals 1. This derivative is also greater than zero at $\Pi \approx$ CONSTANT due to the continuity of the energy function. Therefore, the derivative $\left(\partial U/\partial K\right)_S$ is also positive in the same interval where $\Pi \approx$ CONSTANT (if it was negative, then the energy function would not be continuous). Let us suppose that outside of that interval, $\left(\partial U/\partial K\right)_S$ is negative. This means that at the border of this interval this derivative equals zero, and therefore $\left(\partial U/\partial T\right)_S$ is zero. This cannot happen, because in this case it follows from Eq. (3) that α turns to infinity; hence from Eq. (1) it follows that $\left(\partial T/\partial P\right)_S$ turns to infinity. This contradicts the definition: α is finite. The conclusion can be drown that K and T always increase with U, independent of the sign of α.

It can also be argued that under compression, internal energy increases; part of it becomes a change in kinetic energy, and another part becomes a change in potential energy:

$$\mathrm{d}U = \mathrm{d}U_1 + \mathrm{d}U_2 = \frac{\mathrm{d}K}{\mathrm{d}U_1}\mathrm{d}U_1 + \frac{\mathrm{d}\Pi}{\mathrm{d}U_2}\mathrm{d}U_2 \ .$$

Here, dU_1 and dU_2 are greater than zero and less than dU, and hence dK and dT are always greater than zero. Thus, heat capacity C_S cannot be negative due to the reasons given above.

In the traditional equation for adiabatic compression, $\left(\partial U/\partial T\right)_S$ is positive for positive α, and negative for negative α (Eq. (3)). For some pressures and temperatures, however, α is equal to zero, and hence this derivative is infinite. This is an unphysical result: a small change in the temperature causes an infinite increase in the internal energy. It also follows from Eq. (1) that

$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{\alpha TV}.$$

One can see that for α equal to zero, a small change in the temperature causes an infinite increase in the pressure, and this is unrealistic. The reason for this discrepancy is that the first law of thermodynamics for the *heat exchange* is the following:

$$\delta Q = \mathrm{d}U + P\mathrm{d}V \,. \qquad (6)$$

A quantity of heat δQ is introduced into the system, and this becomes a change in the internal energy and work produced by the system. However, for the heating of a substance *by compression*, the first law of thermodynamics cannot be derived from Eq. (6) and must be derived independently [6–9]:

$$P\mathrm{d}V = -\mathrm{d}U. \qquad (7)$$

The substance is compressed by the work $P\mathrm{d}V$ and this results in a change in internal energy. Heat losses are not taken into account. The sign before $\mathrm{d}U$ in Eq. (7) cannot be theoretically determined; it can only be determined by experiment. Equations (1), (3), (9) and (10) were derived for heat exchange, but not for compression, and cannot be used for the description of adiabatic compression.

Numerous experiments on substances with negative thermal expansion have been performed, and these have shown that heat is expressed under compression [7,9,10,11]. The same experiments with water showed, however, that heat is absorbed under compression in the temperature-pressure interval where water has negative thermal expansion [12–14]. The following explanation can be proposed. Recently, many substances with negative compressibility have been discovered (i.e. they expand under compression) [15–23]. In [7,24,25] it was supposed that water has negative compressibility when it has negative thermal expansion (for pressures of less than 30–60 MPa). This may be the reason why its temperature decreases as the pressure increases.

It is necessary to note that in [26] the compressibility of water from 273 to 373 K and 0 to 100 MPa was determined from sound velocity measurements and was found to be always positive. This was an indirect determination using the following equation:

$$\beta = \frac{V}{c^2} + \frac{T\alpha^2 V}{C_P} \qquad (8)$$

where c is the velocity of sound. However, according to this equation the compressibility of all substances is always positive, which is not the case. Equation (8) is derived from the Mayer's relation and in [27] it was shown that the derivation of the Mayer's relation is wrong.

3. DISCUSSION

It is interesting to consider how enthalpy (heat content) H changes under adiabatic pressure in traditional theory [5]:

$$\left(\frac{\partial H}{\partial P}\right)_S = V \qquad (9)$$

and

$$\left(\frac{\partial H}{\partial T}\right)_S = \frac{C_P}{\alpha T}\,. \qquad (10)$$

At $\alpha < 0$, enthalpy decreases with temperature. This contradicts the physical sense of the process: if the heat content is increased, the temperature must also increase.

Another interesting result follows from Eq. (10) and $\left(\partial H/\partial T\right)_P = C_P$. Due to the continuity of *H*,

$$\operatorname{sign}\left(\frac{\partial H}{\partial T}\right)_{P\approx\mathrm{CONST}} > 0\,.$$

Therefore, in this pressure interval

$$\operatorname{sign}\left[\left(\frac{\partial H}{\partial T}\right)_S\right]_{P\approx\mathrm{CONST}} > 0\,.$$

Let us suppose that outside of this pressure interval where $P \approx$ CONSTANT, the derivative $\left(\partial H/\partial T\right)_S$ is less than zero. This means that at the border of this interval, this derivative is equal to zero, and from Eq. (10) it follows that α turns to infinity. This cannot be true, and it must be concluded that $\left(\partial H/\partial T\right)_S$ is always positive. As mentioned in the previous section, Eqs. (9) and (10) cannot be used for the description of mechanical compression.

4. CONCLUSION

It has been shown that the traditional equations of thermodynamics cannot be used to describe the adiabatic compression of substances because they are derived from the equation which describes heat exchange, Eq. (6). Adiabatic compression is a different process from heat exchange and must be described by other equations. The traditional equations predict that substances with negative thermal expansion absorb heat under compression, while numerous experiments show that they express heat. However, water does absorb heat when it has negative thermal expansion. A possible reason could be that water has negative compressibility in this region, as proposed earlier by the author. As many substances with negative compressibility have been found recently, this explanation appears to be plausible. Direct measurements of compressibility of water were performed at pressures higher than 60 MPa, where thermal expansion and compressibility are positive. Negative compressibility is supposed to take place at pressures lower than 30 MPa for *T* = 270 K and 60 MPa for *T* = 260 K [25]; therefore, precise experiments in this low-pressure region are necessary. Taking the salinity of water into account does not change the results of the theory.

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