## Adiabatic Lapse Rate of Water Is Negative Due to Its Negative Compressibility

# 6 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 always be 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

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The adiabatic lapse rate of water is the rate at which its temperature changes with pressure at constant entropy S, and salinity. According to conventional theory, the adiabatic lapse rate  $(\partial T/\partial P)_s$  is positive if the thermal expansion coefficient  $\alpha$  is positive, and negative for negative

19 values of  $\alpha$  [1–4]: 20

**1. INTRODUCTION** 

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 $\left(\frac{\partial T}{\partial P}\right)_{S} = \frac{\alpha T V}{C_{P}} , \qquad (1)$ 

where *T* is the absolute temperature, *P* is the pressure, *V* is the volume, and *C*<sub>*P*</sub> 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 conclusions of the theory, because the salinity of water is not of primary importance to this problem [1]. However, the derivative of the internal energy *U*,  $(\partial U/\partial P)_s$ , is always positive [1,5]:

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$$\left(\frac{\partial U}{\partial P}\right)_{S} = \frac{\beta C_{V} P V}{C_{P}},$$
 (2)

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

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$$\left(\frac{\partial U}{\partial T}\right)_{S} = \frac{\beta C_{V} P}{\alpha T}.$$
 (3)

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

### 41 2. THEORY

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43 If  $C_{\rm S} < 0$  at  $\alpha < 0$ , then by virtue of Eqs. (1)–(3), the temperature decreases when the internal energy 44 increases. This cannot be true for a substance with positive compressibility, since if a quantity of heat 45  $\delta Q$  is introduced into water at  $\alpha < 0$ , both its internal energy and its temperature increase. According 46 to Joule's principle of equivalence of heat and work, it makes no difference whether the internal 47 energy is increased by introducing a quantity of heat or by compression.

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

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$$U = K + \Pi. \tag{4}$$

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 d*U*:

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$$dU = \left(\frac{\partial U}{\partial K}\right)_{\Pi} dK + \left(\frac{\partial U}{\partial \Pi}\right)_{K} d\Pi \quad .$$
 (5)

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58 The first differential on the right-hand side of Eq. (5) always increases with U. This means that the 59 temperature also increases because the derivative is positive and is equal to 1. This derivative is also 60 greater than zero at  $\Pi \approx \text{CONSTANT}$ , due to the continuity of the energy function. Therefore, the 61 derivative  $(\partial U/\partial K)_s$  is also positive in the same interval where  $\Pi \approx \text{CONSTANT}$  (if it were negative, 62 then the energy function would not be continuous). Let us suppose that outside that interval,  $(\partial U/\partial K)_s$  is negative. This means that at the border of this interval, this derivative equals zero, and 63 therefore  $(\partial U/\partial T)_s$  is zero. This cannot happen, because in this case it follows from Eq. (3) that  $\alpha$ 64 tends to infinity; hence from Eq. (1) it follows that  $(\partial T/\partial P)_s$  tends to infinity. This contradicts the 65 66 definition:  $\alpha$  is finite. The conclusion can be drawn that K and T always increase with U, independent of the sign of  $\alpha$ . 67

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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:

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$$dU = dU_1 + dU_2 = \frac{dK}{dU_1} dU_1 + \frac{d\Pi}{dU_2} dU_2.$$

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.

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In the traditional equation for adiabatic compression,  $(\partial U/\partial T)_s$  is positive for positive values of  $\alpha$ , and negative for negative values of  $\alpha$  (Eq. (3)). For some pressures and temperatures, however,  $\alpha$  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 80

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$$\left(\frac{\partial P}{\partial T}\right)_{S} = \frac{C_{P}}{\alpha T V}.$$

82 One can see that for  $\alpha = 0$ , a small change in the temperature causes an infinite increase in the 83 pressure, and this is unrealistic. The reason for this discrepancy is that the first law of 84 thermodynamics for the *heat exchange* is the following:

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

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]:

$$PdV = -dU.$$
 (7)

The substance is compressed by the work PdV, and this results in a change in internal energy. Heat losses are not taken into account. The sign before dU in Eq. (7) cannot be determined theoretically; 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.

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99 Numerous experiments on substances with negative thermal expansion have been performed, and 100 these have shown that heat is expressed under compression [7,9-11]. The same experiments with water showed, however, that heat is absorbed under compression in the temperature-pressure 101 102 interval where water has negative thermal expansion [12-14]. The following explanation can be 103 proposed. Recently, many substances with negative compressibility have been discovered (i.e. they 104 expand under compression) [15-23]. Some studies have supposed that water has negative 105 compressibility when it has negative thermal expansion (for pressures of less than 30-60 MPa) 106 [7,24,25]. This may be the reason why its temperature decreases as the pressure increases. 107

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

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

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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.

### 118 3. DISCUSSION

120 It is interesting to consider how enthalpy (heat content) *H* changes under adiabatic pressure in
121 traditional theory [5]:
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$$\left(\frac{\partial H}{\partial P}\right)_{S} = V \tag{9}$$

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$$\left(\frac{\partial H}{\partial T}\right)_{S} = \frac{C_{P}}{\alpha T}$$
 (10)

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129 At  $\alpha < 0$ , enthalpy decreases with temperature. This contradicts the physical sense of the process: if 130 the heat content is increased, the temperature must also increase.

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

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$$\operatorname{sign}\left(\frac{\partial H}{\partial T}\right)_{P\approx \text{CONST}} > 0.$$
  
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136 Therefore, in this pressure interval

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

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Let us suppose that outside of this pressure interval where  $P \approx \text{CONSTANT}$ , the derivative  $(\partial H/\partial T)_S$  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  $\alpha$  tends to infinity. This cannot be true, so it must be concluded that  $(\partial H/\partial T)_S$  is always positive. As mentioned in the previous section, Eqs. (9) and (10) cannot be used for the description of mechanical compression.

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#### 147 4. CONCLUSION

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149 It has been shown that the traditional thermodynamic equations cannot be used to describe the 150 adiabatic compression of substances because they are derived from the equation which describes 151 heat exchange, Eq. (6). Adiabatic compression is a different process from heat exchange and must 152 be described by other equations. The traditional equations predict that substances with negative 153 thermal expansion absorb heat under compression, while numerous experiments show that they 154 express heat. However, water does absorb heat when it has negative thermal expansion. A possible 155 reason could be that water has negative compressibility in this region, as proposed earlier by the 156 author. As many substances with negative compressibility have recently been found, this explanation appears to be plausible. Direct measurements of compressibility of water were performed at 157 pressures higher than 60 MPa, where thermal expansion and compressibility are positive. Negative 158 159 compressibility is supposed to take place at pressures lower than 30 MPa for T = 270 K and lower 160 than 60 MPa for T = 260 K [25]; therefore, precise experiments in this low-pressure region are 161 necessary. Taking the salinity of water into account does not change the results of the theory. 162

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