

# Rigorous and General Definition of Thermodynamic Entropy.

## Part II: Temperature of a Thermal Reservoir and Entropy

Gian Paolo Beretta\* and Enzo Zanchini†

**Assumption 1: restriction to normal system.** We call *normal system* any system  $A$  that, starting from every state, can be changed to a non-equilibrium state with higher energy by means of a weight process for  $A$  in which the regions of space  $\mathbf{R}^A$  occupied by the constituents of  $A$  have no net change. From here on, we consider only normal systems.

*Comment.* In traditional treatments of thermodynamics, Assumption 1 is *not stated explicitly, but it is used*, for example when one states that any amount of work can be transferred to a thermal reservoir by a stirrer.

**Theorem 1. Impossibility of a PMM2.** If a normal system  $A$  is in a stable equilibrium state, it is impossible to lower its energy by means of a weight process for  $A$  in which the regions of space  $\mathbf{R}^A$  occupied by the constituents of  $A$  have no net change.

**Proof.** (Figure 1) Suppose that, starting from a stable equilibrium state  $A_{se}$  of  $A$ , by means of a weight process  $\Pi_1$  with positive work  $W^{A\rightarrow} = W > 0$ , the energy of  $A$  is lowered and the regions of space  $\mathbf{R}^A$  occupied by the constituents of  $A$  have no net change. On account of Assumption 1, it would be possible to perform a weight process  $\Pi_2$  for  $A$  in which the regions of space  $\mathbf{R}^A$  occupied by the constituents of  $A$  have no net change, the weight  $M$  is restored to its initial state so that the positive amount of energy  $W^{A\leftarrow} = W > 0$  is supplied back to  $A$ , and the final state of  $A$  is a nonequilibrium state, namely, a state clearly different from  $A_{se}$ . Thus, the zero-work sequence of weight processes  $(\Pi_1, \Pi_2)$  would violate the definition of stable equilibrium state.

**Second Law.** Among all the states of a system  $A$  such that the constituents of  $A$  are contained in a given set of regions of space  $\mathbf{R}^A$ , there is a unique stable equilibrium state for every value of the energy  $E^A$ .

**Lemma 1.** Any stable equilibrium state  $A_s$  of a system  $A$  is accessible via an irreversible zero-work weight process from any other state  $A_1$  with the same regions of space  $\mathbf{R}^A$  and the same value of the energy  $E^A$ .

**Proof.** By the first law and the definition of energy,  $A_s$  and  $A_1$  can be interconnected by a zero-work weight process for  $A$ . However, a zero-work weight process from  $A_s$  to  $A_1$  would violate the definition of stable equilibrium state. Therefore, the process must be in the direction from  $A_1$  to  $A_s$ . The absence of a zero-work weight process in the opposite direction, implies that any zero-work weight process from  $A_1$  to  $A_s$  is irreversible.

**Mutual stable equilibrium states.** We say that two stable equilibrium states  $A_{se}$  and  $B_{se}$  are *mutual stable equilibrium states* if, when  $A$  is in state  $A_{se}$  and  $B$  in state  $B_{se}$ , the composite system  $AB$  is in a stable equilibrium state. The definition holds also for a pair of states of the same system: in this case, system  $AB$  is composed of  $A$  and of a duplicate of  $A$ .

**Thermal reservoir.** We call *thermal reservoir* a closed and always separable system  $R$  with a single constituent, contained in a fixed region of space, with a vanishing external force field, and with values of the energy restricted to a finite range such that all the stable equilibrium states of  $R$  are mutual stable equilibrium states.

*Comment.* Every single-constituent system without internal boundaries and applied external fields, and with a number of particles of the order of one mole (so that the *simple system* approximation as defined in Ref. [1, p.263] applies), when restricted to a fixed region of space of appropriate volume and to the range of energy values corresponding to the so-called *triple-point* stable equilibrium states, is a thermal reservoir.

**Assumption 2. Equivalent thermal reservoirs.** If  $R'$  and  $R''$  are thermal reservoirs with the same constituent, then every stable equilibrium state of  $R'$  is in mutual stable equilibrium with any stable equilibrium state of  $R''$ . Then,  $R'$  and  $R''$  are called *equivalent thermal reservoirs*.

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\*Università di Brescia, Italy, beretta@ing.unibs.it

†Università di Bologna, Italy, enzo.zanchini@unibo.it

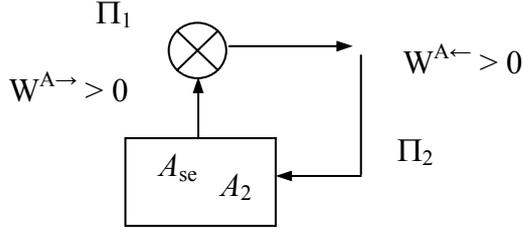


Figure 1: Schematic illustration of the proof of Theorem 1.

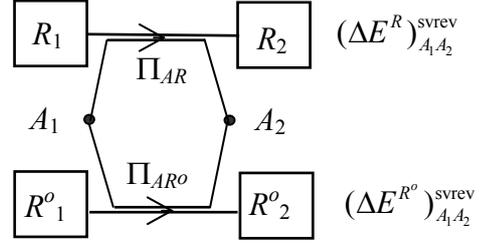


Figure 2: Schematic illustration of the processes used to define the temperature of a thermal reservoir.

**Reference thermal reservoir.** A thermal reservoir with a constituent chosen once and for all, will be called a *reference thermal reservoir*. To fix ideas, we will choose water as the constituent of our reference thermal reservoir.

**Standard weight process.** Given a pair of states  $(A_1, A_2)$  of a system  $A$  and a thermal reservoir  $R$ , we call *standard weight process* for  $AR$  from  $A_1$  to  $A_2$  a weight process for the composite system  $AR$  in which the end states of  $R$  are stable equilibrium states. We denote by  $(A_1 R_1 \rightarrow A_2 R_2)^{sw}$  a standard weight process for  $AR$  from  $A_1$  to  $A_2$  and by  $(\Delta E^R)_{A_1 A_2}^{sw}$  the corresponding energy change of the thermal reservoir  $R$ .

**Assumption 3.** Every pair of states  $(A_1, A_2)$  of a system  $A$  can be interconnected by a reversible standard weight process for  $AR$ , where  $R$  is an arbitrarily chosen thermal reservoir.

**Theorem 2.** For a given system  $A$  and a given reservoir  $R$ , among all the standard weight processes for  $AR$  between a given pair of states  $(A_1, A_2)$  of  $A$ , the energy change  $(\Delta E^R)_{A_1 A_2}^{sw}$  of the thermal reservoir  $R$  has a lower bound which is reached if and only if the process is reversible.

*The proof of Theorem 2 is omitted here, for brevity.*

**Theorem 3.** Let  $R'$  and  $R''$  be any two thermal reservoirs and consider the energy changes,  $(\Delta E^{R'})_{A_1 A_2}^{swrev}$  and  $(\Delta E^{R''})_{A_1 A_2}^{swrev}$  respectively, in the reversible standard weight processes  $\Pi_{AR'} = (A_1 R'_1 \rightarrow A_2 R'_2)^{swrev}$  and  $\Pi_{AR''} = (A_1 R''_1 \rightarrow A_2 R''_2)^{swrev}$ , where  $(A_1, A_2)$  is an arbitrarily chosen pair of states of any closed system  $A$ . Then the ratio  $(\Delta E^{R'})_{A_1 A_2}^{swrev} / (\Delta E^{R''})_{A_1 A_2}^{swrev}$ :

- is positive;
- depends only on  $R'$  and  $R''$ , *i.e.*, it is independent of (i) the initial stable equilibrium states of  $R'$  and  $R''$ , (ii) the choice of system  $A$ , and (iii) the choice of states  $A_1$  and  $A_2$ ;
- is unity if  $R'$  and  $R''$  are equivalent thermal reservoirs.

*The proof of Theorem 3 is omitted here, for brevity.*

**Temperature of a thermal reservoir.** (Figure 2) Let  $R$  be a given thermal reservoir and  $R^o$  a reference thermal reservoir. Select an arbitrary pair of states  $(A_1, A_2)$  of a system  $A$  and consider the energy changes  $(\Delta E^R)_{A_1 A_2}^{swrev}$  and  $(\Delta E^{R^o})_{A_1 A_2}^{swrev}$  in two reversible standard weight processes from  $A_1$  to  $A_2$ , one for  $AR$  and the other for  $AR^o$ , respectively. We call *temperature* of  $R$  the positive quantity

$$T_R = T_{R^o} \frac{(\Delta E^R)_{A_1 A_2}^{swrev}}{(\Delta E^{R^o})_{A_1 A_2}^{swrev}}, \quad (1)$$

where  $T_{R^o}$  is a positive constant associated arbitrarily with the reference thermal reservoir  $R^o$ . If for  $R^o$  we select a thermal reservoir having water as constituent and we set  $T_{R^o} = 273.16$  K, we obtain the Kelvin temperature scale. Clearly, the temperature  $T_R$  of  $R$  is defined only up to an arbitrary multiplicative constant.

**Corollary 2.** The ratio of the temperatures of two thermal reservoirs,  $R'$  and  $R''$ , is independent of the choice of the reference thermal reservoir and can be measured directly as

$$\frac{T_{R'}}{T_{R''}} = \frac{(\Delta E^{R'})_{A_1 A_2}^{swrev}}{(\Delta E^{R''})_{A_1 A_2}^{swrev}}, \quad (2)$$

where  $(\Delta E^{R'})_{A_1 A_2}^{swrev}$  and  $(\Delta E^{R''})_{A_1 A_2}^{swrev}$  are the energy changes of  $R'$  and  $R''$  in two reversible standard weight processes, one for  $AR'$  and the other for  $AR''$ , which interconnect the same pair of states  $(A_1, A_2)$ .

**Proof.** Let  $(\Delta E^{R^o})_{A_1 A_2}^{swrev}$  be the energy change of the reference thermal reservoir  $R^o$  in any reversible standard

weight process for  $AR^o$  which interconnects the same states  $(A_1, A_2)$  of  $A$ . From Eq. (1) we have

$$T_{R'} = T_{R^o} \frac{(\Delta E^{R'})_{A_1 A_2}^{\text{swrev}}}{(\Delta E^{R^o})_{A_1 A_2}^{\text{swrev}}}, \quad T_{R''} = T_{R^o} \frac{(\Delta E^{R''})_{A_1 A_2}^{\text{swrev}}}{(\Delta E^{R^o})_{A_1 A_2}^{\text{swrev}}}, \quad (3)$$

so that the ratio  $T_{R'}/T_{R''}$  is given by Eq. (2).

**Corollary 3.** Let  $(A_1, A_2)$  be any pair of states of system  $A$ , and let  $(\Delta E^R)_{A_1 A_2}^{\text{swrev}}$  be the energy change of a thermal reservoir  $R$  with temperature  $T_R$ , in any reversible standard weight process for  $AR$  from  $A_1$  to  $A_2$ . Then, for the given system  $A$ , the ratio  $(\Delta E^R)_{A_1 A_2}^{\text{swrev}}/T_R$  depends only on the pair of states  $(A_1, A_2)$ , *i.e.*, it is independent of the choice of reservoir  $R$  and of its initial stable equilibrium state  $R_1$ .

**Proof.** Let us consider two reversible standard weight processes from  $A_1$  to  $A_2$ , one for  $AR'$  and the other for  $AR''$ , where  $R'$  is a thermal reservoir with temperature  $T_{R'}$  and  $R''$  is a thermal reservoir with temperature  $T_{R''}$ . Then, equation (2) yields

$$\frac{(\Delta E^{R'})_{A_1 A_2}^{\text{swrev}}}{T_{R'}} = \frac{(\Delta E^{R''})_{A_1 A_2}^{\text{swrev}}}{T_{R''}}. \quad (4)$$

**Definition of (thermodynamic) entropy, proof that it is a property.** Let  $(A_1, A_2)$  be any pair of states of a system  $A$ , and let  $R$  be an arbitrarily chosen thermal reservoir placed in the environment  $B$  of  $A$ . We call *entropy difference* between  $A_2$  and  $A_1$  the quantity

$$S_2^A - S_1^A = -\frac{(\Delta E^R)_{A_1 A_2}^{\text{swrev}}}{T_R} \quad (5)$$

where  $(\Delta E^R)_{A_1 A_2}^{\text{swrev}}$  is the energy change of  $R$  in any reversible standard weight process for  $AR$  from  $A_1$  to  $A_2$ , and  $T_R$  is the temperature of  $R$ . On account of Corollary 3, the right hand side of Eq. (5) is determined uniquely by states  $A_1$  and  $A_2$ ; therefore, entropy is a property of  $A$ .

Let  $A_0$  be a reference state of  $A$ , to which we assign an arbitrarily chosen value of entropy  $S_0^A$ . Then, the value of the entropy of  $A$  in any other state  $A_1$  of  $A$  is determined uniquely by the equation

$$S_1^A = S_0^A - \frac{(\Delta E^R)_{A_1 A_0}^{\text{swrev}}}{T_R}, \quad (6)$$

where  $(\Delta E^R)_{A_1 A_0}^{\text{swrev}}$  is the energy change of  $R$  in any reversible standard weight process for  $AR$  from  $A_0$  to  $A_1$ , and  $T_R$  is the temperature of  $R$ . Such a process exists for every state  $A_1$ , on account of Assumption 3.

**Theorem 4. Additivity of entropy differences.** Consider the pairs of states  $(C_1 = A_1 B_1, C_2 = A_2 B_2)$  of the composite system  $C = AB$ . Then,

$$S_{A_2 B_2}^{AB} - S_{A_1 B_1}^{AB} = S_2^A - S_1^A + S_2^B - S_1^B. \quad (7)$$

**Proof.** Let us choose a thermal reservoir  $R$ , with temperature  $T_R$ , and consider the sequence  $(\Pi_{AR}, \Pi_{BR})$  where  $\Pi_{AR}$  is a reversible standard weight process for  $AR$  from  $A_1$  to  $A_2$ , while  $\Pi_{BR}$  is a reversible standard weight process for  $BR$  from  $B_1$  to  $B_2$ . The sequence  $(\Pi_{AR}, \Pi_{BR})$  is a reversible standard weight process for  $CR$  from  $C_1$  to  $C_2$ , in which the energy change of  $R$  is the sum of the energy changes in the constituent processes  $\Pi_{AR}$  and  $\Pi_{BR}$ , *i.e.*,  $(\Delta E^R)_{C_1 C_2}^{\text{swrev}} = (\Delta E^R)_{A_1 A_2}^{\text{swrev}} + (\Delta E^R)_{B_1 B_2}^{\text{swrev}}$ . Therefore:

$$\frac{(\Delta E^R)_{C_1 C_2}^{\text{swrev}}}{T_R} = \frac{(\Delta E^R)_{A_1 A_2}^{\text{swrev}}}{T_R} + \frac{(\Delta E^R)_{B_1 B_2}^{\text{swrev}}}{T_R}. \quad (8)$$

Equation (8) and the definition of entropy (5) yield Eq. (7).

*Comment.* As a consequence of Theorem 4, if the values of entropy are chosen so that they are additive in the reference states, entropy results as an additive property.

**Theorem 5.** Let  $(A_1, A_2)$  be any pair of states of a system  $A$  and let  $R$  be a thermal reservoir with temperature  $T_R$ . Let  $\Pi_{AR_{\text{irr}}}$  be any irreversible standard weight process for  $AR$  from  $A_1$  to  $A_2$  and let  $(\Delta E^R)_{A_1 A_2}^{\text{swirr}}$  be the energy change of  $R$  in this process. Then

$$-\frac{(\Delta E^R)_{A_1 A_2}^{\text{swirr}}}{T_R} < S_2^A - S_1^A. \quad (9)$$

**Proof.** Let  $\Pi_{AR_{\text{rev}}}$  be any reversible standard weight process for  $AR$  from  $A_1$  to  $A_2$  and let  $(\Delta E^R)_{A_1 A_2}^{\text{swrev}}$  be the energy change of  $R$  in this process. On account of Theorem 2,

$$(\Delta E^R)_{A_1 A_2}^{\text{swrev}} < (\Delta E^R)_{A_1 A_2}^{\text{swirr}}. \quad (10)$$

Since  $T_R$  is positive, from Eqs. (10) and (5) one obtains

$$-\frac{(\Delta E^R)_{A_1 A_2}^{\text{swirr}}}{T_R} < -\frac{(\Delta E^R)_{A_1 A_2}^{\text{swrev}}}{T_R} = S_2^A - S_1^A . \quad (11)$$

**Theorem 6. Principle of entropy nondecrease.** Let  $(A_1, A_2)$  be a pair of states of a system  $A$  and let  $(A_1 \rightarrow A_2)_W$  be any weight process for  $A$  from  $A_1$  to  $A_2$ . Then, the entropy difference  $S_2^A - S_1^A$  is equal to zero if and only if the weight process is reversible; it is strictly positive if and only if the weight process is irreversible.

**Proof.** If  $(A_1 \rightarrow A_2)_W$  is reversible, then it is a special case of a reversible standard weight process for  $AR$  in which the initial stable equilibrium state of  $R$  does not change. Therefore,  $(\Delta E^R)_{A_1 A_2}^{\text{swrev}} = 0$  and by applying the definition of entropy, Eq. (5), one obtains

$$S_2^A - S_1^A = -\frac{(\Delta E^R)_{A_1 A_2}^{\text{swrev}}}{T_R} = 0 . \quad (12)$$

If  $(A_1 \rightarrow A_2)_W$  is irreversible, then it is a special case of an irreversible standard weight process for  $AR$  in which the initial stable equilibrium state of  $R$  does not change. Therefore,  $(\Delta E^R)_{A_1 A_2}^{\text{swirr}} = 0$  and Equation (9) yields

$$S_2^A - S_1^A > -\frac{(\Delta E^R)_{A_1 A_2}^{\text{swirr}}}{T_R} = 0 . \quad (13)$$

Moreover: if a weight process  $(A_1 \rightarrow A_2)_W$  for  $A$  is such that  $S_2^A - S_1^A = 0$ , then the process must be reversible, because we just proved that for any irreversible weight process  $S_2^A - S_1^A > 0$ ; if a weight process  $(A_1 \rightarrow A_2)_W$  for  $A$  is such that  $S_2^A - S_1^A > 0$ , then the process must be irreversible, because we just proved that for any reversible weight process  $S_2^A - S_1^A = 0$ .

## CONCLUSIONS

A general definition of thermodynamic entropy [2] is presented, based on operative definitions of all the concepts employed in the treatment, designed to provide a clarifying and useful, complete and coherent, minimal but general, rigorous logical framework suitable for unambiguous fundamental discussions on Second Law implications.

Operative definitions of system, state, isolated system, environment of a system, process, separable system, and system uncorrelated from its environment are stated, which are valid also in the presence of internal semipermeable walls and reaction mechanisms. The concepts of heat and of quasistatic process are never mentioned, so that the treatment holds also for nonequilibrium states, both for macroscopic and few particles systems.

A definition of thermal reservoir less restrictive than in previous treatments is adopted: it is fulfilled by any single-constituent simple system contained in a fixed region of space, provided that the energy values are restricted to a suitable finite range. The proof that entropy is a property of the system is completed by a new explicit proof that the entropy difference between two states of a system is independent of the initial state of the thermal reservoir chosen to measure it.

The definition of a reversible process is given with reference to a given *scenario*, *i.e.*, the largest isolated system whose subsystems are available for interaction; thus, the operativity of the definition is improved and the treatment becomes compatible also with old [3] and recent [4] interpretations of irreversibility in the quantum theoretical framework.

## References

- [1] E.P. Gyftopoulos and G.P. Beretta, *Thermodynamics. Foundations and Applications*, Dover, Mineola, 2005 (first edition, Macmillan, 1991).
- [2] For the criteria which identify the *entropy of thermodynamics* among the many other concepts also called *entropy*, see E.P. Gyftopoulos and E. Cubukcu, Entropy: Thermodynamic definition and quantum expression, *Phys. Rev. E*, **55**, 3851 (1997).
- [3] See, *e.g.*, G.N. Hatsopoulos and G.P. Beretta, Where is the entropy challenge?, in *Meeting the Entropy Challenge*, AIP Conf. Proc. Series, Vol. **1033**, 2008, p. 34; G.P. Beretta et al., Quantum thermodynamics: a new equation of motion for a single constituent of matter, *Nuovo Cimento B*, **82**, 169 (1984).
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