Outline of Thermodynamics

571R **Laws**[1]
The Zeroth Law, which expresses the transitivity of thermal equilibrium.
The First Law, which is conservation of energy. This allows energy to be used as one of the parameters describing the states of a simple system.
The Second Law. Three popular formulations of this law are:
∗ Clausius: No process is possible, the sole result of which is that heat is transferred from a body to a hotter one.
∗ Kelvin (and Planck): No process is possible, the sole result of which is that a body is cooled and work is done.
∗ Carathéodory: In any neighborhood of any state there are states that cannot be reached from it by an adiabatic process.

572L The first two are not precisely stated due to ambiguous terminologies such as 'hotter', and the last one usually presupposes differentiability.
   The law is really a mathematical theorem about an ordering on a set in terms of a certain kind of preorder[2] denoted by $\prec$ (precedes; can adiabatically go to).

Question
Is there a real-valued function S such that

$$X \prec Y \Rightarrow S(X) \leq S(Y). \tag{1}$$

The function S is also required to be additive and extensive.

572R **Basic concepts**
1. *Thermodynamic system*: The space of states of the system is denoted by a symbol such as Γ and states in Γ by X, Y, Z, etc. A state-space, mathematically, is just a set.
2. *Composition*: The Cartesian product $\Gamma_1 \times \Gamma_2 \equiv \Gamma_1 \times \Gamma_2$ is just another system (called a *compound system*), and points in $\Gamma_1 \times \Gamma_2$ are denoted by pairs (X, Y).[3]
3. *Scaling of states*: For each state-space Γ and number $\lambda > 0$ there is another state-space, denoted by $\Gamma^{(\lambda)}$ with points denoted by λX. This space is called a *scaled copy* of Γ. We
573L identify $\Gamma^{(1)} = \Gamma$ and $1X = X$. We also require $(\Gamma^{(\lambda)})^{(\mu)} = \Gamma^{(\lambda\mu)}$ and $\mu(\lambda X) = (\mu\lambda)X$.[4,5]
4. *Adiabatic accessibility*: We say $X \prec Y$ implies that a state Y is adiabatically accessible from a state X (with X and Y possibly in different state-spaces).
   An *adiabatic process* is a process possible by means of an interaction with some device
573R consisting of some auxiliary system and a weight in such a way that the auxiliary system returns to its initial state at the end of the process, whereas the weight may have risen or

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[1]Main reference: R. Giles, *Mathematical foundations of thermodynamics*, Pergamon, Oxford, 1964.

[2]reflexive, transitive but not antisymmetric.

[3]Physically, it describes two juxtaposed systems. The subsystems comprising a compound system are physically independent systems, but they are allowed to interact with each other for a period of time and thereby to alter each other's state.

[4]The physical interpretation of $\Gamma^{(\lambda)}$ when Γ is the space of one gram of hydrogen is simply the state-space of λ grams of hydrogen with the same intensive properties. We can generalize the above notation to n systems.

[5]The concept of scaling is crucial. It is this concept that makes our thermodynamics inappropriate for microscopic objects like atoms or cosmic objects like stars.

fallen.

Let us write

$$X \prec\prec Y \tag{2}$$

if $X \prec Y$ but not $Y \prec X$ (written $Y \not\prec X$). In this case we say that we can go from X to Y by an irreversible adiabatic process. If $X \prec Y$ and $Y \prec X$, we say that X and Y are *adiabatically equivalent* and write

$$X \overset{A}{\sim} Y. \tag{3}$$

Equivalence classes under $\overset{A}{\sim}$ are called *adiabats*.

5. *Comparability*: Given two states X and Y in two (same or different) state-spaces, we say that they are *comparable* if $X \prec Y$ or $Y \prec X$. This turns out to be a crucial notion. Two states are not always comparable; a necessary condition is that they have the same material composition in terms of the chemical elements.

Entropy principle

There is a real-valued function on all states of all systems (including compound systems) called entropy, denoted by S, such that

a) *Monotonicity*: When X and Y are comparable states, then[6]

$$X \prec Y \iff S(X) \leq S(Y). \tag{6}$$

b) *Additivity* and *extensivity:* If X and Y are states of some (possibly different) systems and if (X, Y) denotes the corresponding state in the compound system, then

$$S(X, Y) = S(X) + S(Y). \tag{7}$$

S is also extensive: for $\lambda > 0$

$$S(\lambda X) = \lambda S(X), \tag{8}$$

Fundamental questions

Q1: Which properties of the relation $\prec$ ensure existence and (essential) uniqueness of S?
Q2: Can these properties be derived from simple physical premises?
Q3: From which premises do convexity and smoothness properties of S follow?
Q4: Can temperature be defined from S, and what are its properties?

Fundamental axioms

The answer to question Q1 can be given by:

A1 Reflexivity. $X \overset{A}{\sim} X$.
A2 Transitivity. If $X \prec Y$ and $Y \prec Z$, then $X \prec Z$.
A3 Consistency. If $X \prec X'$ and $Y \prec Y'$, then $(X, Y) \prec (X', Y')$.
A4 Scaling Invariance. If $\lambda > 0$ and $X \prec Y$, then $\lambda X \prec \lambda Y$.

A5 Splitting and Recombination. $X \overset{A}{\sim} ((1 - \lambda)X, \lambda X)$ for $\lambda \in (0, 1)$.[7]

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[6]If we avoid the notion 'comparable', then we may write

$$X \overset{A}{\sim} Y \Rightarrow S(X) = S(Y), \tag{4}$$
$$X \prec\prec Y \Rightarrow S(X) < S(Y). \tag{5}$$

[7]Note that the state spaces are not the same on both side.

A6 Stability. If $(X, \epsilon Z_0) \prec (Y, \epsilon Z_1)$ for some Z_0 and Z_1 for all sufficiently small ϵ, then $X \prec Y$.

Cancellation Lemma: For any three states X, Y, Z

$$(X, Z) \prec (Y, Z) \Rightarrow X \prec Y. \tag{9}$$

Comparison Hypothesis (CH): For a state-space Γ any pair of states is comparable. Note that the comparability of the states in different state spaces is not implied.

The significance of A1-A6 and CH is borne out by the following theorem:
Theorem 1 [Equivalence of entropy principle and A1-A6, given CH].
The following are equivalent for a state-space Γ:
i) For $X_i, Y_j \in \Gamma$

$$(\lambda_1 X_1, \lambda_2 X_2, \cdots, \lambda_n X_n)) \prec (\mu_1 Y_1, \mu_2 Y_2, \cdots, \mu_m Y_m) \iff \sum_{i=1}^{n} \lambda_i S(X_i) \leq \sum_{i-1}^{m} \mu_i S(Y_i) \tag{10}$$

whenever $\sum \lambda_i = \sum \mu_i$.
ii) The relation $\prec$ satisfies conditions A1-A6, and CH holds for every multiple-scaled copy of Γ.
    This entropy function on Γ is unique up to affine equivalence; i.e., $S(X) \rightarrow aS(X) + B$, with $a > 0$.

That i) $\Rightarrow$ ii) is obvious. The proof of ii) $\Rightarrow$ i) is carried out by an explicit construction of the entropy function on Γ.[8]

Basic Construction of S

Pick two reference points X_0 and X_1 in Γ with $X_0 \prec\prec X_1$.[9] Then define for $X \in \Gamma$

$$S(X) := \sup\{\lambda : ((1 - \lambda)X_0, \lambda X_1) \prec X\}. \tag{11}$$

Remark 1. By A5, $X \overset{A}{\sim} ((1 - \lambda)X, \lambda X)$, and hence, by CH in the space $\Gamma^{(1-\lambda)} \times \Gamma^{(\lambda)}$, X is comparable to $((1 - \lambda)X_0, \lambda X_1)$.
Remark 2. In (11) we allow $\lambda \notin [0, 1]$ by using the convention that

$$(X, -Y) \quad \prec \quad Z \iff X \prec (Y, Z), \tag{12}$$
$$(X, 0Y) \quad = \quad X. \tag{13}$$

Remark 3. For (11) we need to know only that CH holds in twofold scaled products of Γ with itself. CH will then automatically be true for all products.
Remark 4. If we change the two points X_0, X_1 S changes affinely. Choosing the values $S(X_0)$ and $S(X_1)$ (say, 0 and 1, respectively) is equivalent to fixing a and B.

Existence of consistent entropy scale
Theorem 1 extends to products of multiple-scaled copies of different systems, i.e., to general compound systems. This extension is an immediate consequence of the following theorem,

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[8]The logic is reminiscent of an old definition of heat by Laplace and Lavoisier in terms of the amount of ice that a body can melt.

[9]If such points do not exist, then S is the constant function.

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which is proved by applying Theorem 1 to the product of the system under consideration with some standard reference system.

Theorem 2 [Consistent entropy scales]. Assume that CH holds for all compound systems. For each system Γ let S be some definite entropy function on Γ in the sense of Theorem 1. Then there are constants a_Γ and $B(\Gamma)$ such that the function S, defined for all states of all systems by

$$S(X) = a_\Gamma S_\Gamma(X) + B(\Gamma) \tag{14}$$

576L for $X \in \Gamma$, satisfies additivity (7), extensivity (8), and monotonicity (6) in the sense that whenever X and Y are in the same state-space, then

$$X \prec Y \iff S(X) \leq S(Y). \tag{15}$$

Theorem 2 is what we need, except for the question of mixing and chemical reactions.[10]

576R **Demonstration of CH for simple systems**

A *simple system* is one whose state-space can be identified with some open convex subset of some $\boldsymbol{R}^{n+1}$ with a distinguished coordinate denoted by U, called the *energy*, and additional coordinates $V \in \boldsymbol{R}^n$, called *work coordinates*. The first law says that the amount of energy in a state is independent of the manner in which the state was arrived at. CH may be anchored to a few axioms:

A7 Convex combination: If X and Y are states of a simple system and $t \in [0,1]$, then

$$(tX, (1-t)Y) \prec tX + (1-t)Y, \tag{16}$$

in the sense of ordinary convex addition of points in $\boldsymbol{R}^{n+1}$. A straightforward consequence of this axiom (and A5) is that the adiabatically accessible sectors[11] $A_X := \{Y \in \Gamma : X \prec Y\}$ of states X in a simple system Γ are convex sets. Another consequence is a connection between the existence of irreversible processes and Carathéodory's principle.

Lemma 1. Assume A1-A7 for $\Gamma \subset \boldsymbol{R}^{n+1}$ and consider the following statements:

a) Existence of irreversible processes: For every $X \in \Gamma$ there is a $Y \in \Gamma$ with $X \prec\prec Y$.

b) Carathéodory's principle: In every neighborhood of every $X \in \Gamma$ there is a $Z \in \Gamma$ with $X \not\prec Z$.

Then a) $\Rightarrow$ b) always. If the adiabatically accessible sectors in Γ have interior points, then b) $\Rightarrow$ a).

577L We need more postulates:

A8 Irreversibility. For each $X \in \Gamma$ there is a point $Y \in \Gamma$ such that $X \prec\prec Y$.

A9 Lipschitz tangent planes. For each $X \in \Gamma$ the adiabatically accessible sector A_X has a unique support plane at X which is a locally Lipschitz continuous function of X.

A10 Connectedness of the boundary. The boundary ∂A_X (relative to the open set Γ) of every adiabatically accessible sector $A_X \subset \Gamma$ is connected. (This is technical.)

A8 plus Lemma 1 asserts that every X lies on the boundary ∂A_X of its adiabatically accessible sector. Although A9 only asserts that the convex set A_X has a true tangent at X, it is an easy consequence of A2 that A_X has a true tangent everywhere on its boundary. To say that

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[10]As long as we do not consider adiabatic processes in which systems are converted into each other (e.g., a compound system consisting of a vessel of hydrogen and a vessel of oxygen is converted into a vessel of water), the entropy principle has been verified.

[11]called forward sectors in the original paper.

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this tangent plane is locally Lipschitz continuous means that

$$\frac{\partial U}{\partial V_j}(V) = -P_j(U(V), V) \tag{17}$$

for $j = 1, \cdots, n$ not only have a solution (since we know that the surface ∂A_X exists) but this solution must be unique. Thus, if $Y \in \partial A_X$, then $X \in \partial A_Y$. In short, the surfaces ∂A_X foliate the state-space Γ.

What is less obvious but very important because it instantly gives us CH for Γ is the following.

Theorem 3 [adiabatically accessible sectors are nested]. If A_X and A_Y are two adiabatically accessible sectors in the state-space of a simple system, then exactly one of the following holds:

a) $A_X = A_Y$, i.e., $X \overset{A}{\sim} Y$.
b) $A_X \subset (A_Y)^\circ$, i.e., $Y \prec\prec X$.
c) $A_Y \subset (A_X)^\circ$, i.e., $X \prec\prec Y$.

It can also be shown from our axioms that the orientation of adiabatically accessible sectors with respect to the energy axis is the same for all simple systems. By convention we choose the direction of the energy axis so that the energy always increases in adiabatic processes at fixed work coordinates.

Theorem 3 implies that the $\overset{A}{\sim}$ equivalence classes consist of the boundaries of adiabatically accessible sets. Carathéodory uses Frobenius' theorem plus assumptions about dif-

ferentiability to conclude the existence locally of a surface containing X. Important global information, such as Theorem 3, is then not easy to obtain without further assumptions.

Although we have established CH for a simple system, Γ, we have not yet established CH even for a product of two copies of Γ. This is needed in the definition of S given in (11). We need five more postulates.

Axioms of thermal contact

In order to relate systems to each other in the hope of establishing CH for compounds and thereby an additive entropy function, some way must be found to put them into contact

with each other. This is the thermal contact. To formalize it we need:

A11 Thermal contact. For any two simple systems with state-spaces Γ_1 and Γ_2 there is another simple system, called the thermal join of Γ_1 and Γ_2, with state-space

$$\Delta_{12} = \{(U, V_1, V_2) : U = U_1 + U_2 \text{ with } (U_1, V_1) \in \Gamma_1, (U_2, V_2) \in \Gamma_2\}. \tag{18}$$

Moreover,

$$\Gamma_1 \times \Gamma_2 \ni ((U_1, V_1), (U_2, V_2)) \prec (U_1 + U_2, V_1, V_2) \in \Delta_{12}. \tag{19}$$

A12 Thermal splitting. For any point $(U, V1, V2) \in \Delta_{12}$ there is at least one pair of states, $(U_1, V_1) \in \Gamma_1, (U_2, V_2) \in \Gamma_2$, with $U = U_1 + U_2$, such that

$$(U, V1, V2) \overset{A}{\sim} ((U1, V1), (U2, V2)). \tag{20}$$

If $(U, V1, V2) \overset{A}{\sim} ((U1, V1), (U2, V2))$, we say that the states $X = (U_1, V_1)$ and $Y = (U_2, V_2))$ are in thermal equilibrium and write

$$X \overset{T}{\sim} Y. \tag{21}$$

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A13 Zeroth law of thermodynamics. If $X \overset{T}{\sim} Y$ and if $Y \overset{T}{\sim} Z$, then $X \overset{T}{\sim} Z$.

A11 and A12 together say that for each choice of the individual work coordinates there is a way to divide up the energy U between the two systems in a stable manner. A12 is the stability statement, for it says that joining is reversible. This reversibility allows us to think of the thermal join, which is a simple system in its own right, as a special subset of the product system $\Gamma_1 \times \Gamma_2$ which we call the *thermal diagonal*. In particular, A12 allows us to prove easily that $X \overset{T}{\sim} \lambda X$ for all X and all $\lambda > 0$.

A14 Transversality.[12] If Γ is the state-space of a simple system and if $X \in \Gamma$, then there exist states $X_0 \overset{T}{\sim} X_1$ with $X_0 \prec\prec X \prec\prec X_1$.

A14 requires that for every adiabat there exists at least one isotherm containing points on both sides of the adiabat.[13]

A15 Universal temperature range. If Γ_1 and Γ_2 are state-spaces of simple systems, then, for every $X \in \Gamma_1$ and every V belonging to the projection of Γ_2 onto the space of its work coordinates, there is a $Y \in \Gamma_2$ with work coordinates V such that $X \overset{T}{\sim} Y$.[14]

With these axioms we can establish CH for products of simple systems (each of which satisfies CH, as we already know). First, the thermal join establishes CH for the (scaled) product of a simple system with itself. The basic idea here is that the points in the product that lie on the thermal diagonal are comparable, since points in a simple system are comparable. In particular, with X, X_0, X_1 as in A14, the states $((1-\lambda)X_0, \lambda X_1)$ and $((1-\lambda)X, \lambda X)$ can be regarded as states of the same simple system and are therefore comparable. This is the key point needed for the construction of S, according to (11).

With some more work we can establish CH for multiple-scaled copies of a simple system.

CH for compound systems and universal entropy

The next task is to show that the multiplicative constants can be adjusted to give a universal entropy valid for copies of different systems, i.e., to establish the hypothesis of Theorem 2. This is based on the following.

Lemma 2 [Existence of calibrators]. If Γ_1 and Γ_2 are simple systems, then there exist states $X_0, X_1 \in \Gamma_1$ and $Y_0, Y_1 \in \Gamma_2$ such that $X_0 \prec\prec X_1$ and $Y_0 \prec\prec Y_1$ and $(X_0, Y_1) \overset{A}{\sim} (X_1, Y_0)$.

The significance of Lemma 2 is that it allows us to fix the multiplicative constants by the condition

$$S_1(X_0) + S_2(Y_1) = S_1(X_1) + S_2(Y_0). \tag{22}$$

The proof of Lemma 2 is complicated and really uses all the axioms A1 to A14. With its aid we arrive at our chief goal, which is CH for compound systems.

Theorem 4 [Entropy principle in products of simple systems].

CH is valid in arbitrary scaled products of simple systems. Hence, by Theorem 2, the relation $\prec$ among states in such state-spaces is characterized by an entropy function S. The entropy function is unique, up to an overall multiplicative constant and one additive constant for

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[12]A14 implies A8.

[13]Note that, for each given X, only two points in the entire state-space Γ are required to have the stated property. This assumption essentially prevents a state-space from breaking up into two pieces that do not communicate with each other. Without it, counterexamples to CH for compound systems can be constructed.

[14]A15 is technical and perhaps can be eliminated. Its physical motivation is that a sufficiently large copy of a system can act as a heat bath for other systems. This postulate is needed if we want to be able to bring every system into thermal equilibrium with every other system.

each simple system under consideration.

Temperature
Concavity of S (implied by A7), Lipschitz continuity of the pressure, and the transversality condition, together with some real analysis, answer Q3 and Q4.

Theorem 5 [Entropy defines temperature]. The entropy S is a concave and continuously differentiable function on the state-space of a simple system. If the function T is defined by

$$\frac{1}{T} := \left.\frac{\partial S}{\partial U}\right|_V, \tag{23}$$

then $T > 0$ and T characterizes the relation $\overset{T}{\sim}$ in the sense that $X \overset{T}{\sim} Y \iff T(X) = T(Y)$. Moreover, if two systems are brought into thermal contact with fixed work coordinates, then, since the total entropy cannot decrease, the energy flows from the system with the higher T to the system with the lower T.

580L **Mixing and Chemical Reactions**[15]
One can formulate the problem as the determination of the additive constants $B(\Gamma)$ of Theorem 2. Oddly, this determination turns out to be far more complex mathematically and physically than the determination of the multiplicative constants.[16]

What we already know is that every system has a well-defined entropy function, e.g., for each Γ there is S_Γ and we know from Theorem 2 that the multiplicative constants a_Γ can be determined in such a way that the sum of the entropies increases in any adiabatic process in any compound space $\Gamma_1 \times \Gamma_2 \times \cdots$. Thus, if $X_i \in \Gamma_i$ and $Y_i \in \Gamma_i$, then

$$(X_1, X_2, \cdots) \prec (Y_1, Y_2, \cdots) \iff \sum S_i(X_i) \leq \sum S_j(Y_j), \tag{24}$$

where we have denoted $S_i = S_{\Gamma_i}$ for short. The additive entropy constants do not matter here, since each function S_i appears on both sides of this inequality.

The task is to find constants $B(\Gamma)$, one for each state-space Γ, in such a way that the entropy defined by

$$S(X) := S_\Gamma(X) + B(\Gamma) \tag{25}$$

for $X \in \Gamma$ satisfies

$$S(X) \leq S(Y) \tag{26}$$

whenever

$$X \prec Y \text{ with } X \in \Gamma, Y \in \Gamma'. \tag{27}$$

Moreover, we require that the newly defined entropy satisfy scaling and additivity under composition. Since the initial entropies $S(X)$ already satisfy them, these requirements become conditions on the additive constants $B(\Gamma)$:

$$B(\Gamma^{(\lambda)} \times \Gamma'^{(\mu)}) = \lambda B(\Gamma) + \mu B(\Gamma'). \tag{28}$$

We wish to define the *minimum entropy change* required from Γ to Γ': $F(\Gamma, \Gamma')$. These are built up from simpler quantities

$$D(\Gamma, \Gamma') := \inf\{S_{\Gamma'}(Y) - S_\Gamma(X) : X \in \Gamma, Y \in \Gamma', X \prec Y\}. \tag{29}$$

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[15]which are not really different, as far as thermodynamics is concerned.

[16]In traditional treatments one usually resorts to gedanken experiments involving 'semipermeable membranes', etc., but they are avoided.

If there is no adiabatic process leading from X to Y, $D = +\infty$.

Next, for any given Γ and Γ', we consider all finite chains of state-spaces $\Gamma = \Gamma_1, \Gamma_2, \cdots, \Gamma_N = \Gamma'$ such that $D(\Gamma_i, \Gamma_{i+1}) < +\infty$ for all i, and define

$$E(\Gamma, \Gamma') := \inf\{D(\Gamma_1, \Gamma_2) + \cdots + D(\Gamma_{N-1}, \Gamma_N)\}, \tag{30}$$

where the infimum is taken over all such chains linking Γ and Γ'. This defines the minimum entropy change along any path connecting Γ to Γ'.

Now, we should allow contact with other systems during the process so long as their state at the beginning and the end of the process are identical (catalysts). Therefore, the general definition of F is

$$F(\Gamma, \Gamma') := \inf_{\Gamma_0}\{E(\Gamma \times \Gamma_0, \Gamma' \times \Gamma_0)\}. \tag{31}$$

Theorem 6 [Constant entropy differences]. If Γ and Γ' are two state-spaces, then for any two states $X \in \Gamma$ and $Y \in \Gamma'$

$$X \prec Y \iff S_\Gamma(X) + F(\Gamma, \Gamma') \leq S_{\Gamma'}(Y). \tag{32}$$

An essential ingredient for the proof of this theorem is (24).

According to Theorem 6 the determination of the entropy constants $B(\Gamma)$ amounts to satisfying the inequalities

$$-F(\Gamma', \Gamma) \leq B(\Gamma) - B(\Gamma') \leq F(\Gamma, \Gamma') \tag{33}$$

together with the linearity condition (28). It is clear that (33) can only be satisfied with finite constants $B(\Gamma)$ and $B(\Gamma')$ if $F(\Gamma, \Gamma') > -\infty$. To exclude the pathological case $F(\Gamma, \Gamma') = -\infty$, we introduce A16, whose statement requires the following definition.

Definition. A state-space Γ is said to be *connected* to another state-space Γ' if there are states $X \in \Gamma$ and $Y \in \Gamma'$, and state-spaces $\Gamma_1, \cdots, \Gamma_N$ with states $X_i, Y_i \in \Gamma_i$ $(i = 1, \cdots, N)$, and a state-space Γ_0 with states $X_0, Y_0 \in \Gamma_0$, such that

$$(X; X_0) \prec Y_1, Y_i \prec Y_{i+1}(i = 1, \cdots, N-1), X_N \prec (Y; Y_0). \tag{34}$$

A16 Absence of sinks. If Γ is connected to Γ', then Γ' is connected to Γ.

This axiom excludes $F(\Gamma, \Gamma') = -\infty$, because, on general grounds, one always has

$$-F(\Gamma', G) \leq F(\Gamma, \Gamma'). \tag{35}$$

Hence $F(\Gamma, \Gamma') = -\infty$ (which means, in particular, that Γ is connected to Γ') would imply $F(\Gamma', \Gamma) = \infty$, i.e., that there is no way back from Γ' to Γ. This is excluded by A16.

The quantities $F(\Gamma', \Gamma)$ have simple subadditivity properties that allow us to use the Hahn-Banach theorem to satisfy the inequalities (33), with constants $B(\Gamma)$ that depend linearly on Γ, in the sense of (28). Hence we arrive at

Theorem 7 [Universal entropy]. The additive entropy constants of all systems can be calibrated in such a way that the entropy is additive and extensive and $X \prec Y$ implies $S(X) \leq S(Y)$, even when X and Y do not belong to the same state-space.

Our final remark concerns the remaining non-uniqueness of the constants $B(\Gamma)$. This indeterminacy can be traced back to the nonuniqueness of a linear functional lying between

$-F(\Gamma', .\Gamma)$ and $F(\Gamma, \Gamma')$ and has two possible sources: one is that some pairs of state-spaces Γ and Γ' may not be connected; i.e., $F(\Gamma, \Gamma')$ may be infinite (in which case $F(\Gamma', \Gamma)$ is also infinite by A16). The other is that there might be a true gap; i.e.,

$$-F(\Gamma', \Gamma) < F(\Gamma, \Gamma') \tag{36}$$

581R   might hold for some state-spaces, even if both sides are finite.

In nature only states containing the same amount of the chemical elements can be transformed into each other. Hence $F(\Gamma, \Gamma') = +\infty$ for many pairs of state-spaces, in particular, for those that contain different amounts of some chemical element. The constants $B(\Gamma)$ are, therefore, never unique: For each equivalence class of state-spaces (with respect to the relation of connectedness) one can define a constant that is arbitrary except for the proviso that the constants should be additive and extensive under composition and scaling of systems.

In our world there are 92 chemical elements,[17] and this leaves us with at least 92 free constants that specify the entropy of one gram of each of the chemical elements in some specific state.

The other possible source of nonuniqueness, a nontrivial gap (36) for systems with the same composition in terms of the chemical elements, is, as far as we know, not realized in nature.[18] Hence, once the entropy constants for the chemical elements have been fixed and a temperature unit has been chosen (to fix the multiplicative constants), the universal entropy is completely fixed.

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[17]or, strictly speaking, a somewhat larger number, since one should count different isotopes as different elements.

[18]Note that this assertion can be tested experimentally without invoking semipermeable membranes.