To summarize, the main conclusion so far is:

The existence and (essential) uniqueness of entropy is **equivalent** to the (very natural) assumptions A1-A6 about the relation of adiabatic accessibility plus the comparison property, CP.

However, CP is not at all self evident, as can be seen by considering systems where “rubbing” and “thermal equilibration” are the only adiabatical operations.

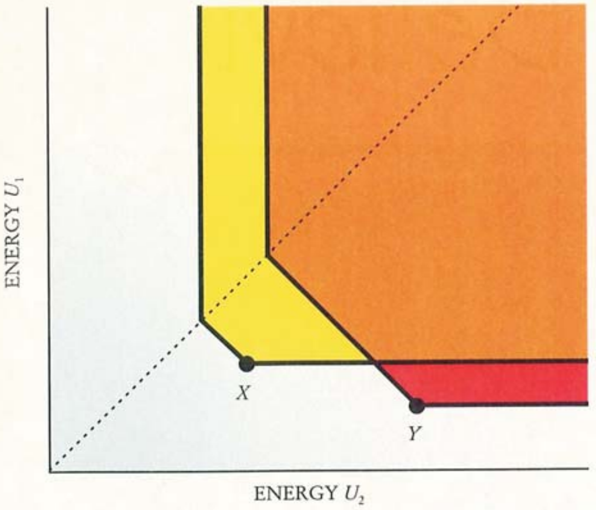


FIGURE 4. HYPOTHETICALLY NONCOMPARABLE STATES. The graph shows the state space of a pair of identical, incompressible solids with the energies U_1 and U_2 as the only coordinates of the compound system. The states adiabatically accessible from X (yellow/orange) and Y (red/orange) are shown under the assumption that the only adiabatic changes consist in combinations of rubbing (increasing U_1 or U_2) and thermal equilibration (moving to the diagonal $U_1 = U_2$). In this example, adiabatic accessibility *cannot* be characterized by an entropy function, because neither a transformation from X to Y nor from Y to X is possible. The comparison hypothesis does not hold here. In the real world, however, it *always* holds.

An essential part of our analysis is a derivation of CP from additional assumptions about **SIMPLE SYSTEMS** which are the basic building blocks of thermodynamics. At the same time we make contact with the traditional concepts of thermodynamic like pressure and temperature.

The states of simple systems are described by one **energy coordinate**, the internal energy, U, (the **First Law** enters here) and one or more **work coordinates**, like the volume V. (Note: U, V are *fundamental* (not (P, V) or (P, T)), etc.)

Thus the state space of a simple system is no longer just an abstract set but a concrete subset of an $\mathbb{R}^{1+n}$.

FIRST LAW OF THERMODYNAMICS

If the state of a system is changed in an adiabatic process, i.e., such that the only net effect in the surroundings is the raising or lowering of a weight, then the energy delivered or received by the weight depends only on the initial and the final state of the system.

The internal energy $U(X)$ is defined by measuring the energy change with respect to some reference state X_0 in a process that either takes $X_0 \to X$ or $X \to X_0$.

We now assume (A1)-(A6), and for simple systems in addition the following

SIMPLE SYSTEM AXIOMS

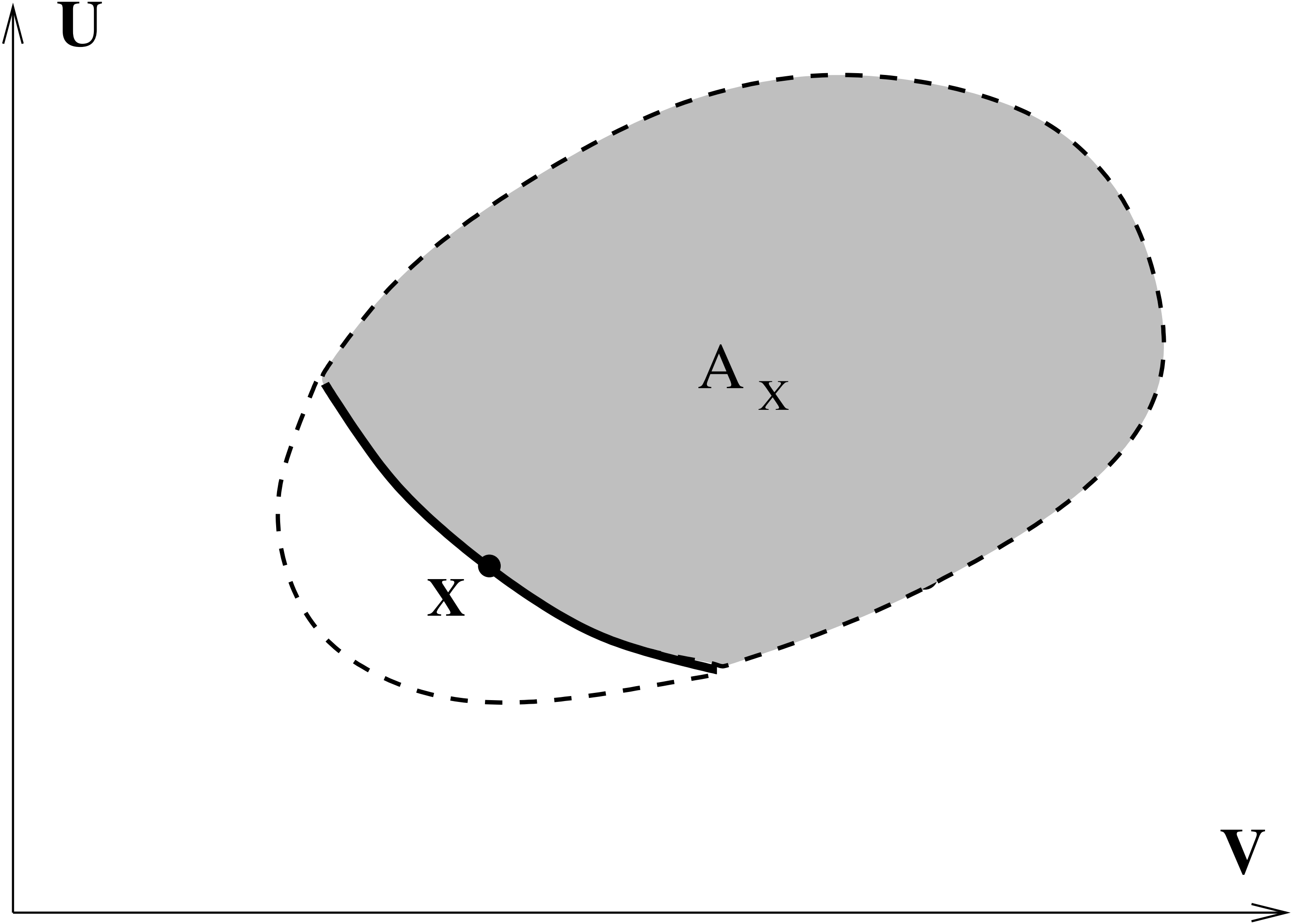
S1. Convex Combination:

$$((1-\lambda)X, \lambda Y) \prec (1-\lambda)X + \lambda Y.$$

(This implies that the **forward sector**

$$A_X = \{Y \in \Gamma : X \prec Y\}$$

is a *convex* set.)


U
A
X
X
V

S2. **Existence of irreversible processes**: For every X there is a Y with $X \prec\prec Y$.

Given the other axioms this is equivalent to Carathéodory's principle: In every neighbourhood of every $X \in \Gamma$ there is a $Z \in \Gamma$ with $X \not\prec Z$. It also implies that every X lies on the boundary of its forward sector.

S3. Tangent planes: For every $X \in \Gamma$ the (convex!) forward sector $\mathcal{A}_X$ has a unique support plane at X. If $X = (U^0, V^0)$ then this plane is given by

$$U - U^0 + P(X) \cdot (V - V^0) = 0.$$

P is called the **PRESSURE** and it is assumed to be locally **Lipschitz continuous**:

$$|P(X) - P(Y)| \leq C|X - Y|.$$

S4. **Connectedness of boundary**: The boundary $\partial\mathcal{A}_X$ of each forward sector $\mathcal{A}_X$ is connected.

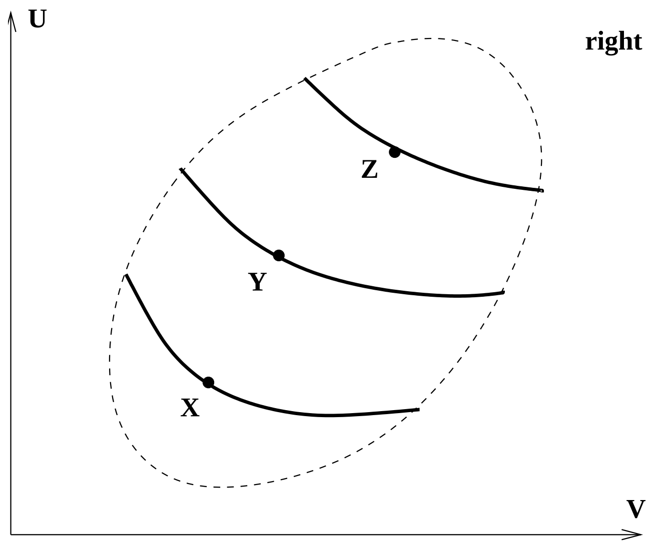
Lipschitz continuity and connectedness imply that the boundary $u(V)$ of $\partial\mathcal{A}_X$ is given by the unique solution to the differential equation

$$\frac{\partial u(V)}{\partial V} = -P(u(V), V).$$

From these assumptions the main theorem about simple systems can be proved:

THEOREM 3 (Comparability for simple systems)
If X *and* Y *are two states of a simple system,* Γ*, then either* $X \prec Y$*, or* $Y \prec X$*. Moreover,*

$$X \overset{\mathrm{A}}{\sim} Y \Longleftrightarrow Y \in \partial \mathcal{A}_X \Longleftrightarrow X \in \partial \mathcal{A}_Y$$


U
right
Z
Y
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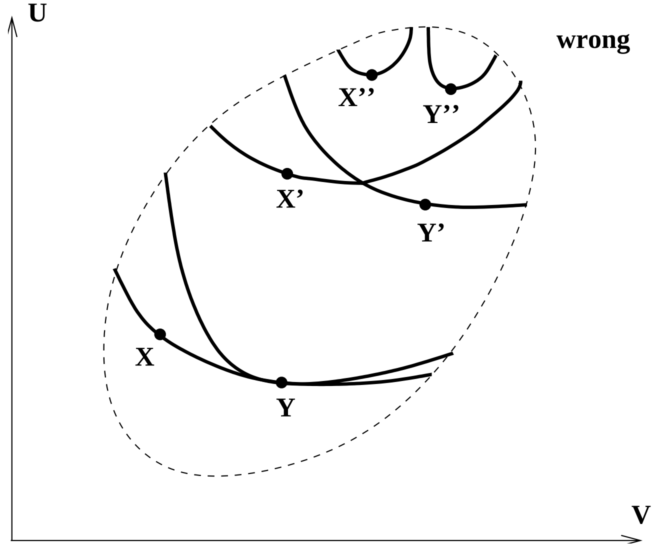
U
wrong
X''
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X'
Y'
X
Y
V

To define S, however, comparability of the states in Γ is not enough. We need more, namely comparability on $(1-\lambda)\Gamma \times \lambda\Gamma$ for all $\lambda \in [0, 1]$!

For this we shall appeal to **THERMAL CONTACT** established for instance by connecting the systems via a copper thread. This produces a new simple system out of two others,. Applying the previous results to this system will then imply comparability also for the product of the two systems.

We now formalize this idea by making four assumptions.

T1. Thermal join: For any two simple systems with state-spaces Γ_1 and Γ_2, there is another *simple* system, called their thermal join, with state space

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

If $X = (U_1, V_1) \in \Gamma_1$, and $Y = (U_2, V_2) \in \Gamma_2$ we define

$$\theta(X, Y) := (U_1 + U_2, V_1, V_2) \in \Delta_{12}.$$

It is assumed that the formation of a thermal join is an adiabatic operation for the compound system, i.e.,

$$(X, Y) \prec \theta(X, Y).$$

T2. **Thermal splitting:** For any point $Z \in \Delta_{12}$ there is at least one pair of states, $X \in \Gamma_1$, $Y \in \Gamma_2$, such that

$$Z = \theta(X, Y) \overset{\mathsf{A}}{\sim} (X, Y)$$

DEFINITION. If $\theta(X, Y) \overset{\mathsf{A}}{\sim} (X, Y)$ we say that the states X and Y are in **thermal equilibrium** and write

$$X \overset{\mathsf{T}}{\sim} Y.$$

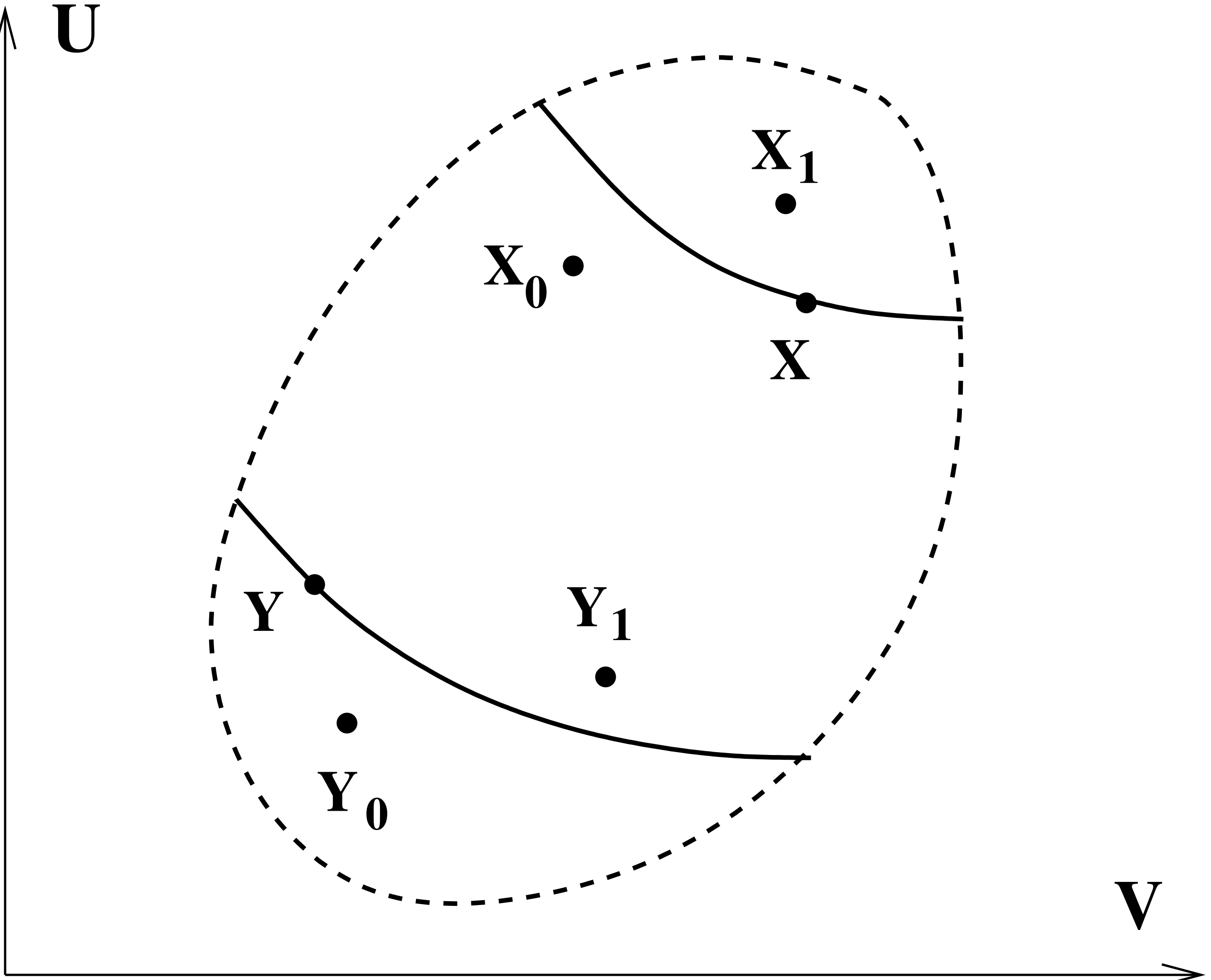
S1 and S2 together say that for each choice of the individual work coordinates there is a way to divide up the energy U between the two systems in a stable manner. S2 is the stability statement, for it says that joining is reversible, i.e., once the equilibrium has been established, one can cut the copper thread and retrieve the two systems back again, but with a special partition of the energies.

T3. Zeroth law: $X \overset{\mathrm{T}}{\sim} Y$ and $Y \overset{\mathrm{T}}{\sim} Z \Rightarrow X \overset{\mathrm{T}}{\sim} Z$.

The equivalence classes w.r.t. the relation $\overset{\mathrm{T}}{\sim}$ are called **isotherms**.

T4. **Transversality**: If Γ is the state space of a simple system and if $X \in \Gamma$, then there exist states $X_0 \overset{\mathrm{T}}{\sim} X_1$ with $X_0 \prec\prec X \prec\prec X_1$.

Intuitively this says that adiabats and isotherms do not coincide.


U
X_1
X_0
X
Y
Y_1
Y_0
V

With these axioms one establishes comparison for compound systems, which is needed for the construction of S and the consistent adjustment of entropy units for different systems to ensure additivity.

The *key point* is that the states $((1-\lambda)X_0, \lambda X_1)$ and $X \overset{\mathrm{A}}{\sim} ((1-\lambda)X, \lambda X)$ can be regarded as states of the same simple system (the thermal join of $(1-\lambda)\Gamma$ and $\lambda\Gamma$) and are hence comparable, by Theorem 2.

THEOREM 4 (Thermal contact implies CP.) *The comparison property holds for arbitrary scaled products of simple systems. Hence the relation $\prec$ in such state spaces is characterized by an additive and extensive entropy, S. The entropy is unique up to an overall multiplicative constant and one additive constant for each 'basic' simple system.*

Moreover, the entropy is a concave function of the energy and work coordinates (by S1), and it is nowhere locally constant (by S2).

The uniqueness is very important! It means that entropy can be determined in the usual way from heat capacities, compressibilities etc by integration:

$$S(X) - S(X_0) = \int_{X_0 \to X} \frac{dU + PdV}{T}.$$

But first we must define T!

THEOREM 5 (Entropy defines temperature.) *The entropy, S, is a continuously differentiable function on the state space of a simple system. If the function T is defined by*

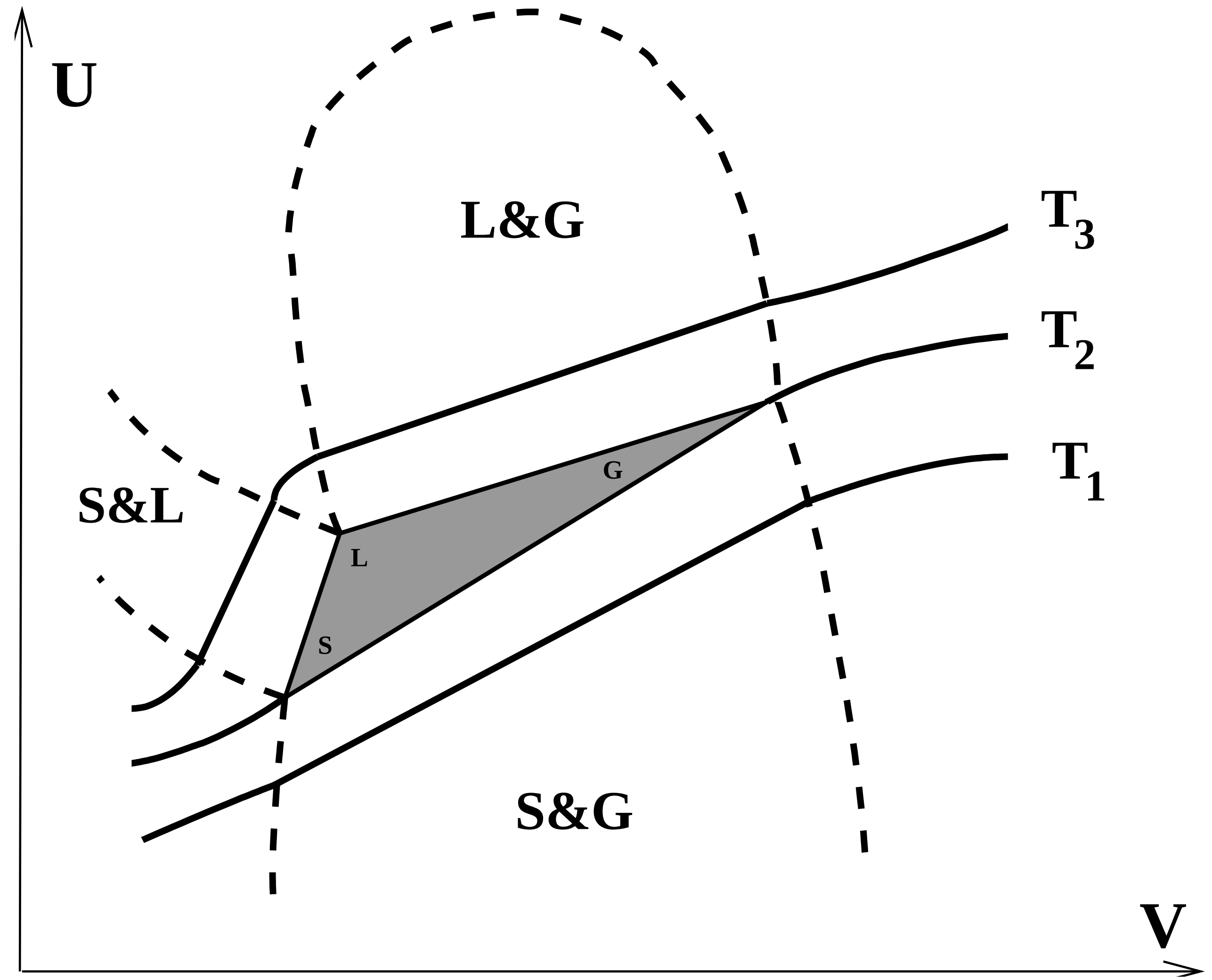
$$1/T = \left(\frac{\partial S}{\partial U}\right)_V$$

then T characterizes the relation $\overset{T}{\sim}$ in the sense that

$$X \overset{T}{\sim} Y \Leftrightarrow T(X) = T(Y).$$

Moreover, if two systems are brought into thermal contact with fixed work coordinates, then energy flows from the system with higher value T to the system with lower value of T.

REMARK While adiabats, i.e., the level sets of S, are convex hypersurfaces, the isotherms can be much more complicated.


U
L&G
T$_3$
T$_2$
T$_1$
S&L
G
L
S
S&G
V

MIXTURES AND CHEMICAL REACTIONS

The problem is to choose the entropy constants for different chemical compounds and mixtures in a consistent way.

Usual approach: appeal to ‘semipermeable membranes’ that don’t really exist in nature.

Can be avoided!

But need one more axiom:

M1 (Absence of sinks): If Γ and Γ' are state spaces such that $X \prec Y$ for some $X \in \Gamma$, $Y \in \Gamma'$, then $Z \prec W$ for some $Z \in \Gamma'$, $W \in \Gamma$.

THEOREM 6. (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.*

CONCLUSIONS

A line of thought that can be traced back to C. Carathéodory, P.-T. Landsberg, H.-A. Buchdahl, G. Falk, P. Jung and R. Giles has led to an axiomatic foundation for thermodynamics.

What, if anything, has been gained compared to the usual approaches involving concepts like 'quasi-static processes', 'heat' and 'Carnot machines' on the one hand and statistical mechanics on the other hand?

1) It is not necessary to introduce intuitive concepts like 'heat', 'hot', 'cold', 'quasi-static processes' nor 'semipermeable membranes' as primitive concepts. Also 'temperature' becomes a derived concept.

2) In order to define entropy, there is no need for special machines and processes on the empirical side, and there is no need for assumptions about models on the statistical mechanical side. Entropy is seen as a codification of possible state changes that can be accomplished without changing the rest of the universe in any way except for moving a weight.

Just as energy conservation was eventually seen to be a consequence of time translation invariance, in like manner *entropy can be seen to be a consequence of some simple properties of the list of state pairs related by adiabatic accessibility*.

If the second law can be demystified, so much the better. If it can be seen to be a consequence of simple, plausible notions then, as Einstein said, it cannot be overthrown.

SOME APPLICATIONS OF ENTROPY

1. THE CARNOT LIMIT ON EFFICIENCY

Define a **thermal reservoir** to by a system with fixed work coordinates and so large that its temperature can be taken to be independent of the energy.

If the energy of a reservoir changes by ΔU_{res}, the entropy change is therefore

$$\Delta S_{\text{res}} = \frac{\Delta U_{\text{res}}}{T_{\text{res}}}$$

Consider now two reservoirs with temperatures $T_h > T_\ell > 0$ and a machine that couples to the reservoirs in a cyclic process, delivering the work (mechanical energy) W in each cycle.

By the First Law

$$\Delta U_h + \Delta U_\ell + W = 0$$

and by the Second Law

$$\Delta S_h + \Delta S_\ell \geq 0$$

i.e.

$$\frac{\Delta U_h}{T_h} + \frac{\Delta U_\ell}{T_\ell} \geq 0.$$

Since $\Delta U_h < 0$ and $T_\ell > 0$ this implies

$$\frac{\Delta U_\ell}{\Delta U_h} \leq -\frac{T_\ell}{T_h}.$$

The **efficiency** is defined as

$$\eta = \frac{W}{-\Delta U_h} = \left(1 + \frac{\Delta U_\ell}{\Delta U_h}\right)$$

and we obtain

$$\eta \leq \eta_C := \left(1 - \frac{T_\ell}{T_h}\right).$$

2. AVAILABLE ENERGY (EXERGY)

Consider the surrounding of a system as a reservoir of temperature T_0. How much work can be extracted from system+surrounding if the system ends up at temperature T_0 with energy U_0 and entropy S_0?

First law:

$$\Delta U + \Delta U_{\text{res}} + W = 0.$$

Second law:

$$\Delta S + \Delta S_{\text{res}} \geq 0.$$

Now

$$\Delta S_{\text{res}} = \frac{\Delta U_{\text{res}}}{T_0}$$

so the 1st and 2nd laws imply

$$\Delta S - \frac{\Delta U - W}{T_0} \geq 0,$$

or, with $\Delta U = U_0 - U$, $\Delta S = S_0 - S$,

$$W \leq (U - U_0) - T_0(S - S_0) =: \Phi.$$

The quantity Φ is called **available energy** or **exergy**.

REMARKS

1. Φ depends both on the system and the surrounding.

2. The energy difference $U - U_0$ can have either sign, but Φ is always nonnegative! (By concavity of entropy.)

3. In the example of the iceberg in the Gulf Stream, $U - U_0 < 0$, but Φ is positive because the loss of energy is outweighed by the negative $T_0(S - S_0)$.

3. EQUATIONS OF STATE

The **thermal equation(s) of state**

$$P = P(T, V)$$

and the **caloric equation of state**

$$U = U(T, V)$$

describe the properties of a simple thermodynamic system.

The latter gives the **heat capacity at constant volume**

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V .$$

The former gives the **isothermal compressibility**

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

and the **thermal expansion coefficient**

$$\alpha_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_V .$$

Both equations of state follow from the **fundamental equation**

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

by differentiation:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V \Rightarrow U = U(T, V)$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_U \Rightarrow P = U(T, V).$$

We say that S **as a function of its natural variables** (U, V) is a **thermodynamic potential**.

It is a remarkable consequence of the fundamental equation that the equations of state are not independent.

Their connection is derived as follows:

First write dS in the variables (T, V):

$$\begin{aligned} dS &= \frac{1}{T}\left[\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV\right] + \frac{P}{T} dV \\ &= \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV. \end{aligned}$$

Then use that dS is a **total differential**, which implies

$$\frac{\partial}{\partial V}\left[\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V\right] = \frac{\partial}{\partial T}\left[\frac{1}{T}\left(\left(\frac{\partial U}{\partial V}\right)_T + P\right)\right].$$

Carrying out the differentiations gives

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

4. FROM EMPIRICAL TO ABSOLUTE TEMPERATURE

Any state function Θ that is constant on each isotherm but has different values on different isotherms is called an **empirical temperature**.

Thus Θ is a strictly monotone function of T alone; we assume it to be differentiable.

The connection between the caloric and thermal equations of state allows us to compute the inverse function $T = T(\Theta)$ from directly measurable quantities.

First note that by the chain rule

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial P}{\partial \Theta}\right)_V \frac{d\Theta}{dT}.$$

Inserted into the connection between the caloric and thermal equations of state gives a differential equation for $T = T(\Theta)$:

$$\left(\frac{\partial U}{\partial V}\right)_{\Theta} = T\left(\frac{\partial P}{\partial \Theta}\right)_V \frac{d\Theta}{dT} - P.$$

that can be rewritten

$$\frac{1}{T}\frac{dT}{d\Theta} = \frac{\left(\frac{\partial P}{\partial \Theta}\right)_V}{P + \left(\frac{\partial U}{\partial V}\right)_{\Theta}}.$$

The solution is

$$T(\Theta) = T_0 \exp\left(\int_{\Theta_0}^{\Theta} \frac{\left(\frac{\partial P}{\partial \Theta'}\right)_V}{P + \left(\frac{\partial U}{\partial V}\right)_{\Theta'}} \, d\Theta' \right)$$

where the choice of $T_0(\Theta_0)$ fixes the temperature unit.

Standard choice: $T_0 = 273,16$ K if Θ_0 corresponds to the triple point of water.

5. IDEAL GASES

An ideal gas is, by definition, a system such that

- $\frac{PV}{Rn} = T_{\text{gas}}$ is an empirical temperature (with n the mole number and R such that $T_0 = 273,16$ K at the triple point of water.) (Boyle's law.)

- T_{gas} is independent of volume if the energy is constant (Guy-Lussac law).

The first equation gives

$$\left(\frac{\partial P}{\partial T_g}\right)_V = \frac{P}{T_g}$$

and the second

$$\left(\frac{\partial U}{\partial V}\right)_{T_{\mathsf{gas}}} = -\frac{\left(\frac{\partial T_{\mathsf{gas}}}{\partial V}\right)_U}{\left(\frac{\partial T_{\mathsf{gas}}}{\partial U}\right)_V} = 0$$

Insertion into the formula for $T(\Theta)$ with $\Theta = T_{\mathsf{gas}}$ gives

$$T = T_{\mathsf{gas}}$$

6. COMPUTATION AND MEASUREMENT OF ENTROPY

In the variables (T, V) the fundamental equation is

$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV.$$

Using the connection between the caloric and thermal equations of state and the definition of the heat capacity C_V we can write this as

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV.$$

This form is very useful for the determination of S in practice by integration along a suitable path. Heat capacities and $(\partial P/\partial T)_V$ are also directly measurable.

For an ideal gas with a constant heat capacity we obtain as an example

$$S(T,V) = C_V \ln(T/T_0) + nR \ln(V/V_0).$$