Supplemental Material for the Article: *Work Storage in States of Apparent Negative Thermodynamic Temperature* [Phys. Rev. Lett. (2018)]

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This supplemental material reviews elements of thermodynamics to provide additional background for the discussion in the main paper. In particular, we review:

Section I: Mathematical formulation of 1st and 2nd law of thermodynamics; Clausius, Kelvin-Planck, Stability statements, discussed for their meaning, and evaluated with the laws of thermodynamics.

Section II: Processes in chemically metastable systems, and work storage in these systems.

Section III: A simple quantum model with apparent negative temperature is used to discuss some behavior of such systems.

I. 2ND LAW STATEMENTS

To provide background for the main paper [1], we review various statements of the 2nd law of thermodynamics, as well as the notions of equilibrium states, and temperature. The next section states the 1st and 2nd law of thermodynamics in mathematical form, which were constructed to be in agreement with the various verbal formulations of the second law that can be found anywhere in the literature. The subsequent sections present these statements, and discusses them in their meaning, and within the context of the mathematical formulations of the laws.

A. 1st and 2nd Law of Thermodynamics

For a clear distinction of the different verbal formulations of the *2nd Law of Thermodynamics*, its mathematical form is required, along with the *1st Law of Thermodynamics*, which states conservation of energy. We present the laws in a form typically found for the case of closed systems (no exchange of mass), where they read [2]:

1st law: Conservation of Energy

$$\frac{dE}{dt}=\sum_k \dot{Q}_k-\sum_j \dot{W}_j \tag{1}$$

Here, $E=U+E_{mech}$ is the energy of the system, which is the sum of the internal (or thermal) energy of the system, U, and its mechanical energy, E_{mech}, which accounts for, e.g., the kinetic energy in the center of mass frame, E_{kin} (think of coffee swirling in the cup after stirring), or the potential energy, E_{pot}, etc., stored in the system. Since the system is closed, its energy can only change due to transfer of energy as heat, with contributions $\dot{Q}_k$, or as power, with contributions $\dot{W}_j$. Engineering sign convention is used, where heat *into* the system and work done *by* the system are positive.

2nd law: Balance of Entropy

$$\frac{dS}{dt}+\sum \beta_k \dot{Q}_k=\dot{S}_{gen}\geq 0 \tag{2}$$

Here, S is the entropy of the system, and $\beta_k=-\frac{1}{T_k}$ is a measure for the thermodynamic temperature at that system boundary where the heat $\dot{Q}_k$ is transferred across the boundary; $-\beta_k\dot{Q}_k$ is the entropy flux across that boundary. Moreover, $\dot{S}_{gen}$ is the generation rate of entropy within the system boundaries which vanishes in equilibrium, and is positive in non-equilibrium processes.

The use of β instead of the thermodynamic temperature T is common, and useful, in the discussion of thermodynamic temperature and its sign; classical positive temperature implies negative values of β while negative thermodynamic temperature implies positive β.

We note that the laws of thermodynamics are valid in equilibrium and non-equilibrium situations, that is at all times the system possesses definite amounts of energy and entropy. For equilibrium states energy and entropy can be easily related to measurable properties such as temperature, pressure or volume through material dependent property relations [2], while for non-equilibrium states one might not have explicit expressions for these.

We refer to Boltzmann's kinetic theory as an example for a description (of an ideal gas) that is accessible to arbitrarily strong non-equilibria, and is accompanied by laws such as the above at all times [5].

B. Approach to Equilibrium

> *An isolated thermodynamic system will over time approach a unique and stable equilibrium state, and remain in that state indefinitely* [2, 3].

We shall discuss stability of the equilibrium state with the other statements below. For an isolated system, all exchange of heat and work vanishes, $\dot{Q}_k=\dot{W}_j=0$, so that total energy stays constant, $\frac{dE}{dt}=0$, and the 2nd law reduces to

$$\frac{dS}{dt}=\dot{S}_{gen}\geq 0 \tag{3}$$

The latter equation states that in the isolated system entropy will grow until it reaches a maximum compatible

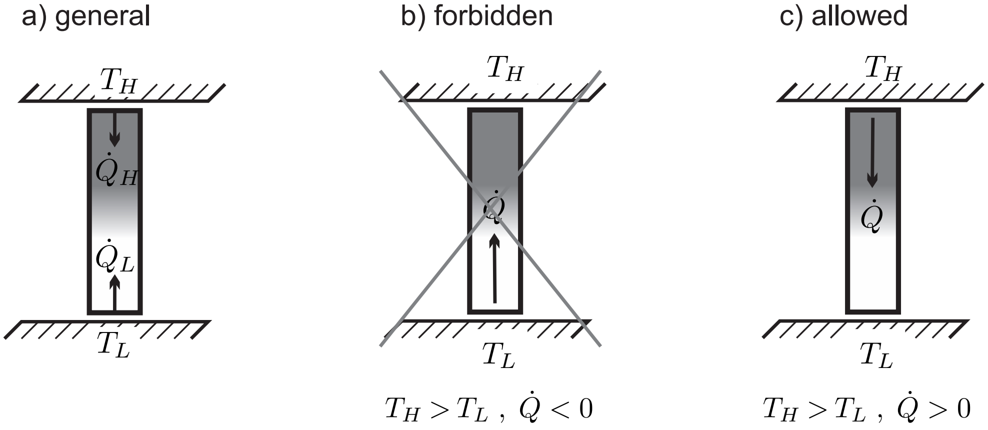

FIG. 1: Illustration of the Clausius statement: Heat conductor between two reservoirs at temperatures T_H and T_L. a) General set-up: heat into the conductor is indicated as positive, the 1st law of thermodynamics gives $\dot{Q}_L = -\dot{Q}_H = -\dot{Q}$; b) Forbidden process: spontaneous heat transfer from cold to hot; c) Allowed process: spontaneous heat transfer from hot to cold.

with the fixed energy E and the fixed mass m of the system. In the final equilibrium state the entropy generation vanishes, $\dot{S}_{gen} = 0$, and the system remains at this state as long as it remains isolated.

It is a classical subject of thermodynamics to show that in the final equilibrium state temperature, pressure and chemical potential are homogeneous, and kinetic energy vanishes [2].

A more careful discussion of stability will follow below. We point out already here, that the stable equilibrium state as defined above requires that the mechanical (i.e., kinetic, potential, etc.) energy of the system assumes a minimum–which is the stable equilibrium state for the mechanical degrees of freedom. A system might be trapped in an elevated mechanical state, e.g., by fixing an upside down pendulum, by spanning and clamping a spring, or by putting a weight into a bowl. A state is considered stable, when after a disturbance, the system will return to the initial state. A disturbance removing the ficture of the pendulum, pushing the spring out of the clamp, or pushing the ball over the edge of the bowl, will lead to a different state, which is the final stable equilibrium state.

C. Clausius Statement

> *Heat cannot pass spontaneously from a body of lower temperature to a body of higher temperature* [2, 3, 6].

This statement is based on daily experience. The Clausius Statement implies that heat might indeed pass spontaneously from a body of higher temperature to a body of lower temperature. The forbidden and the allowed process are indicated in Figs. 2b/c.

In particular, the Clausius statement implies the thermal stability of the equilibrium state, where temperature is homogeneous. Indeed, would a small fluctuation of temperature occur in a body at equilibrium, and would heat spontaneously flow from cold to hot, then the fluctuation would grow, and the temperature become inhomogeneous.

To consider the statement in the light of the above formulations of 1st and 2nd law (1, 2), we apply these to a closed system which acts as heat conductor between two thermal reservoirs at temperatures $T_H = -\frac{1}{\beta_H}$ and $T_L = -\frac{1}{\beta_L}$ (see Fig. 2a). When the process runs at steady state, and the heat conductor is in mechanical equilibrium, we have $\frac{dU}{dt} = \frac{dS}{dt} = E_{mech} = \dot{W}_j = 0$, and the laws reduce to

$$0 = \dot{Q}_H + \dot{Q}_L \quad , \quad \beta_H \dot{Q}_H + \beta_L \dot{Q}_L = \dot{S}_{gen} \geq 0 \tag{4}$$

From the 1st law we find $\dot{Q}_H = -\dot{Q}_L = \dot{Q}$, hence the 2nd law reduces to

$$(\beta_H - \beta_L)\,\dot{Q} = \dot{S}_{gen} \geq 0\ . \tag{5}$$

According to the Clausius statement, heat goes from hot (H) to cold (L), and not vice versa, therefore we must have $\dot{Q} > 0$, so that the inequality demands $(\beta_H - \beta_L) > 0$. Hence, hotter states have larger value of the temperature parameter β. From this statement follows no restriction for the sign of $\beta = -\frac{1}{T}$, negative T are not excluded. Since β grows with hotness, it is clear that states of negative T are considered to be hotter, for the Clausius statement to be valid [7].

We note that the thermal reservoirs are assumed to be in stable equilibrium states, but the heat conductor—the system to which we apply the laws of thermodynamics—is in an inhomogeneous non-equilibrium state.

While the direction of spontaneous heat transfer is restricted, no such restriction exists for the transfer of work: gears and levers can be used to transfer work in any direction. Hence, the 2nd law contains only the entropy flux term $\sum \beta_k \dot{Q}_k$, which ensures the direction of heat transfer, and has no counterpart for work (which

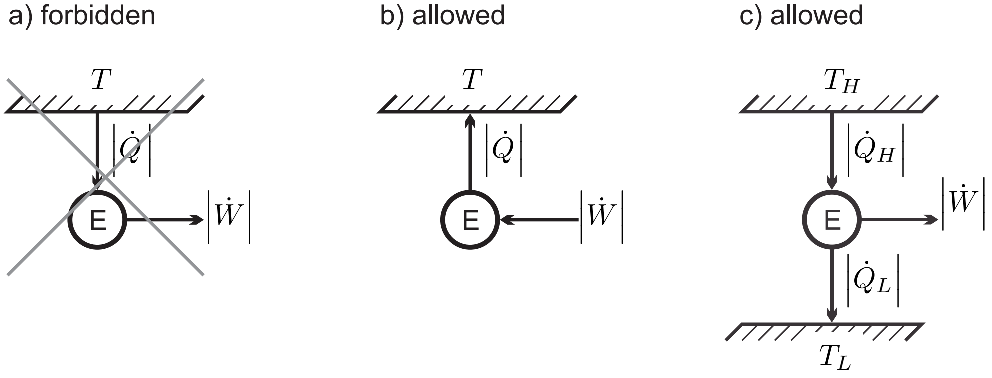

FIG. 2: Illustration of the Kelvin-Planck statement: Engine E in heat transfer contact with one or two reservoirs. Transfer direction for heat and work is indicated by arrows. a) Forbidden proces: full conversion of heat into work; b) Allowed process: full dissipation of work into heat; c) Allowed process: conversion of some of the heat flowing between two reservoirs to work..

could be, e.g., a term $\sum \gamma_j \dot{W}_j$; careful reasoning shows $\gamma_j = 0$ [2]).

D. Thermodynamic driving forces

Let us consider the Clausius statement in light of the stated trend for equilibration: As soon as we connect the two equilibrium reservoirs at T_H and T_L through the heat conductor, we have created a larger system, consisting of two reservoirs and the heat conductor, which is in a non-equilibrium state: the temperature of the compound system is inhomogeneous. The heat transfer through the conductor is the compound system's attempt to reach an equilibrium state of uniform temperature: The heat transfer process is driven by the desire to equilibrate.

Using the language of irreversible thermodynamics [4] we can say that the non-equilibrium state, here the temperature difference, provides a *thermodynamic force* that drives a *thermodynamic process*, the transfer of energy as heat [4].

Indeed, all thermodynamic processes are driven by thermodynamic forces of some kind, which induce the processes such that the system moves towards equilibrium.

E. Kelvin-Planck statement

> *It is impossible to construct an engine that will work in a complete cycle and produce no effect except the raising of a weight* [i.e., produce work] *and the transfer of energy out of a system* [e.g., a reservoir] *in a stable equilibrium state* [3].

The above is the formulation of Gyftopoulos & Beretta, which explicitely clarifies that the system providing energy is in stable equilibrium, and does not specify how energy is drawn form the reservoir (which could be heat or work). Ramsey expresses the Kelvin-Planck statement with less detail as

> *It is impossible to construct an engine that will operate in a closed cycle and produce no effect other than the extraction of heat from a reservoir with the performance of an equivalent amount of work* [7].

The discussion of negative thermodynamic temperature in the framework of the 2nd law concentrates on the Kelvin-Planck statement [7], although the actual processes that are performed in the experiments are adiabatic, that is the inverted quantum states are reached by work interaction; processes like these will be discussed in the next section.

Similar to our discussion of the the Clausius statement, we include in the discussion not only what the Kelvin-Planck statement forbids, but also what it allows. While the direct conversion of heat to work is forbidden, the full conversion of work to heat is allowed—this simply describes heating through friction.

Also, while work cannot be obtained from a single reservoir, the statement allows that work can be obtained from two reservoirs at different temperatures. According to the Clausius statement, heat will flow from the hotter to the colder reservoir. The Kelvin-Planck statement allows that some of the heat can be converted to work.

Figure 2 shows the three processes, one forbidden (a), two allowed (b, c), which we discuss now by means of the laws of thermodynamics.

The engine runs at steady state, hence for the interaction with a single reservoir (Fig. 2a/b) at temperature $T = -\frac{1}{\beta}$, the thermodynamic laws reduce to

$$0 = \dot{Q} - \dot{W} \quad , \quad \beta \dot{Q} = \dot{S}_{gen} \geq 0 \ . \tag{6}$$

With the engineering sign convention used, the Kelvin-Planck statement forbids positive work (i.e., work done *by* the engine), but allows negative work (i.e., work done

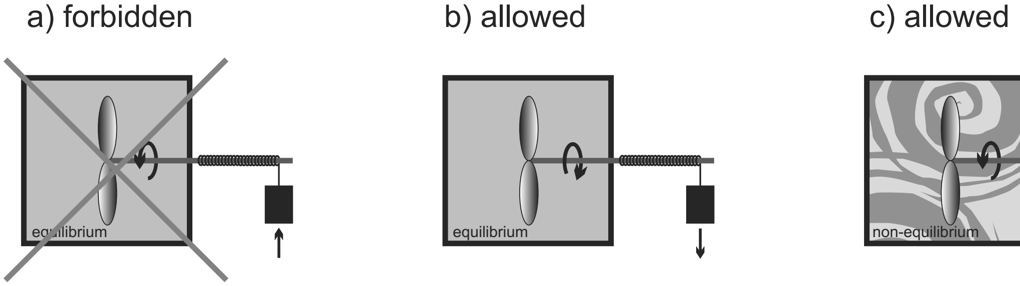

FIG. 3: Illustration of the Stability Statement: An equilibrium system, confined in an adiabatic rigid container, cannot lift a weight (a), but can disspate work done on the paddle wheel by a falling weight (b). Work to lift the weight can be obtained from a non-equilibrium state or an unstable state, such as a swirling motion of a fluid (c).

to the engine), so that

$$\dot{Q} = \dot{W} < 0 \quad , \quad \beta\dot{W} = \dot{S}_{gen} \geq 0 \ . \tag{7}$$

Accordingly, the Kelvin-Planck statement requires negative β, or positive thermodynamic temperature of the reservoir,

$$\beta = -\frac{1}{T} < 0 \quad \Longrightarrow \quad T > 0 \ . \tag{8}$$

For the interaction with two reservoirs (Fig. 2c), 1st and 2nd law reduce to

$$0 = \dot{Q}_H + \dot{Q}_L - \dot{W} \quad , \quad \beta_H \dot{Q}_H + \beta_L \dot{Q}_L = \dot{S}_{gen} \geq 0 \ . \tag{9}$$

Eliminating the heat $\dot{Q}_L$, we find the work that can be obtained as

$$\dot{W} = \left(1 - \frac{\beta_H}{\beta_L}\right)\dot{Q}_H - \frac{\dot{S}_{gen}}{-\beta_L} = \left(1 - \frac{T_L}{T_H}\right)\dot{Q}_H - T_L \dot{S}_{gen} \ . \tag{10}$$

With thermodynamic temperature being positive, this result leads to well known conclusion that no heat engine operating between two reservoirs can have an efficiency above the Carnot efficiency $\eta_C = \frac{\dot{W}}{\dot{Q}_H} = 1 - \frac{T_L}{T_H}$, and that any irreversible processes occurring within the engine (so that $\dot{S}_{gen} > 0$) reduces the work output.

We included the last result into the discussion to emphasize that, while work cannot be obtained from a single reservoir, one can obtain work from two reservoirs. As was seen in the discussion of the Clausius statement, there is a desire for equilibration between two reservoirs in non-equilibrium, at different temperatures, which provides the driving force for the heat flow. The discussion above shows that work can be obtained from the heat flowing from hot to cold. It follows that non-equilibrium provides the driving force for harvesting work from the system.

F. Ramsey's extension of the Kelvin-Planck statement

> *It is impossible to construct an engine that will operate in a closed cycle and produce no effect other than . . . (2) the rejection of heat into a negative-temperature reservoir with the corresponding work being done on the engine.* [7]

For his extension of the Kelvin-Planck statement, Ramsey allowed for thermodynamic temperature to be negative, i.e., $\beta > 0$, and kept the mathematical formulations of the 1st and 2nd law unchanged. For this case, instead of (7), one finds

$$\beta > 0 \quad , \quad \beta\dot{Q} = \dot{S}_{gen} \geq 0 \quad \Rightarrow \quad \dot{Q} = \dot{W} > 0 \ . \tag{11}$$

Hence, for $\beta > 0$, the heat into the engine must be positive, that is the reservoir can only provide heat, but not receive heat.

While Ramsey formulated the extension as a negative statement (*. . . impossible. . .*), one reads off (11) that the stament *allows* to produce work ($\dot{W} > 0$) from a single reservoir (in stable equilibrium!) at negative temperature; there is no discernible driving force for such a process.

We close with the comment that if one finds a reservoir-like system that allows to produce work without a driving force, the original Kelvin-Planck law would lead to the conclusion that the system is not in a stable equilibrium state, while the Ramsey extension would lead to the conclusion that the system's thermodynamic temperature is negative. This is further discussed in the next section.

G. Stability Statement

> *It is impossible to produce work by reducing the energy of a system existing in stable thermodynamic equilibrium and confined within a rigid adiabatic container.* [6]

This statement is typically illustrated with a paddle wheel and a weight, see Fig. 3: One will not expect that in a system in stable equilibrium the molecular motion will suddenly be such that the paddle wheel will move, and lift a weight (a), while work done to the paddle wheel from a falling weight can be absorbed in the system (b).

However, if the system is in a non-equilibrium state or in an unstable equilibrium state, in the figure indicated by a swirling motion, work could be extracted (c).

At closer inspection, the stability statement guarantees the mechanical stability of the equilibrium state: For a classical system, such as a liquid or a gas, a small fluctuation in velocity will not build up and develop into a macroscopic motion of the system. Such a motion could lead to macroscopic kinetic energy that can be harvested as work by the paddle wheel as in Fig. 3c, or to a build-up in pressure that could be harvested as work by a moving piston within the system (which is a rigid adiabatic container).

Application of the 1st and 2nd law to the adiabatic system in a rigid container yields at first ($\dot{Q}_k = 0$)

$$\frac{dU_E}{dt} = -\dot{W} \quad , \quad \frac{dS_E}{dt} = \dot{S}_{gen} \geq 0 \ , \tag{12}$$

where the index E indicates equilibrium states, as explicitly mentioned in the statement. Note that in equilibrium mechanical energy vanishes, $E_{mech|E} = 0$.

Further conclusions about temperature require the Gibbs equation, which provides a universally valid relation between thermodynamic properties in equilibrium states. For simple systems (i.e., no change of composition) it reads $TdS_E = dU_E + p_E dV$ where p_E is the equilibrium pressure of the system, and V is system volume [2].

Using the Gibbs equation to combine the two laws (for constant volume), we find

$$\begin{aligned} \frac{dS_E}{dt} &= \left(\frac{\partial S_E}{\partial U_E}\right)_V \frac{dU_E}{dt} = -\left(\frac{\partial S_E}{\partial U_E}\right)_V \dot{W} \\ &= -\frac{\dot{W}}{T} = \beta \dot{W} = \dot{S}_{gen} \geq 0 \ . \end{aligned} \tag{13}$$

The stability statement forbids positive work, hence we must have $\dot{W} < 0$, which implies that the inequality demands positive values of system temperature: $\left(\frac{\partial S_{|E}}{\partial U_E}\right)_V = \frac{1}{T} = -\beta > 0$. The above discussion links the sign of thermodynamic temperature to mechanical stability: only if the thermodynamic temperature is positive will the system remain in the mechanical equilibrium state.

Note that the overall conclusion agrees with that from the Kelvin-Planck statement: thermodynamic temperature is positive, and it is not possible to draw work from a single reservoir (stable equilibrium), i.e., without a driving force [10].

If the liquid is in thermal equilibrium, but not in mechanical equilibrium (i.e., $E_{mech} \neq 0$), and the system does not exchange work or heat with its environment, the first law gives $\frac{dU_E}{dt} = -\frac{dE_{mech}}{dt}$, and the second law demands that

$$\left(\frac{\partial S_E}{\partial U_E}\right)_V \frac{dU_E}{dt} = -\left(\frac{\partial S_E}{\partial U_E}\right)_V \frac{dE_{mech}}{dt} \geq 0 \ . \tag{14}$$

For instance, with $E_{mech} = E_{pot}$, the weight connected to the paddle wheel in Fig. 3, will fall (Fig. 3b), $\frac{dE_{pot}}{dt} < 0$, only if $T > 0$. The driving force of the process is, again, equilibration, here to reach the mechanical ground state where the weight assumes the lowest possible position.

We consider the mechanical non-equilibrium case of Fig. 3c, where the fluid is in a swirling motion with kinetic energy E_{kin}. We assume thermal equilibrium, so that 1st and 2nd law read

$$\frac{d\left(U_E + E_{kin}\right)}{dt} = -\dot{W} \quad , \quad \frac{dS_E}{dt} = \dot{S}_{gen} \geq 0 \ . \tag{15}$$

Combining the laws by means of the relation $\left(\frac{\partial S_E}{\partial U_E}\right)_V = \frac{1}{T}$, which is valid in thermal equilibrium, shows that work can be obtained from the decrease of kinetic energy,

$$\dot{W} = -\frac{dE_{kin}}{dt} - T\dot{S}_{gen} \ . \tag{16}$$

Entropy generation reduces the amount of work that can be obtained. In case that no work is harvested, we simply find the dissipation of kinetic energy until it vanishes in equilibrium, expressed as $\frac{dE_{kin}}{dt} = -T\dot{S}_{gen} \leq 0$.

II. CHEMICALLY UNSTABLE EQUILIBRIUM STATES

For the discussion of chemically unstable states we consider a reacting mixture, such as oxygen, hydrogen and water vapor, which might be found either in stable chemical equilibrium, or trapped in an unstable state. Phase changes can be considered as reactions, hence phase changes such as between diamond and graphite are included in this discussion as well. The following is valid for any kind of mixture, constitutive equations are not required. We assume thermal and mechanical equilibrium, so that temperature and pressure are homogeneous.

A. Gibbs equation for mixtures

For simplicity, we restrict the discussion to systems where pressure, temperature, and chemical composition are controlled. The Gibbs equation for the mixture in thermal and mechanical equilibrium reads [2]

$$TdS = dH - Vdp - \sum_\alpha \mu_\alpha dn_\alpha \tag{17}$$

where p, T, V are pressure, temperature and volume of the mixture, $S = \sum_\alpha n_\alpha s_\alpha$ is its total entropy and $H = \sum_\alpha n_\alpha h_\alpha$ is its internal energy; here, μ_α, s_α, h_a denote the chemical potential, entropy and enthalpy of component α. Moreover, n_α is the mole number of component α, and the mole fraction of the component is $X_\alpha = \frac{n_\alpha}{n}$ with $n = \sum n_\alpha$ and $\sum X_\alpha = 1$. We consider closed systems in homogeneous states only, where mole numbers can only change due to chemical reaction, or phase change.

For a single reaction mechanism, mole numbers change as

$$dn_\alpha = \gamma_\alpha d\Lambda \tag{18}$$

where γ_α denotes the stoichiometric coefficients, and Λ counts the number of reactions taking place. The reaction can proceed forwards or backwards, that is $d\Lambda$ can be postivie or negative.

Then, the Gibbs equation for the mixture assumes the form

$$TdS = dH - Vdp - \sum_\alpha \gamma_\alpha \mu_\alpha \, d\Lambda \tag{19}$$

Next, we differentiate between cases where the mixture is in stable chemical equilibrium at all times, and cases where the mixture is trapped in an unstable state, out of stable chemical equilibrium.

B. Stable chemical equilibrium

The equilibrium states that are assumed in the discussion of the 2nd law include chemical equilibrium, for which the law of mass action is found as [2]

$$\sum_\alpha \gamma_\alpha \mu_\alpha = 0 \quad \text{(chemical equilibrium)} \tag{20}$$

For a system where temperature and volume is controlled, this follows from minimization of Gibbs free energy $G = H - TS$ at constant pressure and temperature [2]. According to the law of mass action, the mole numbers n_α are not independently controlled, but related to temperature and pressure. With (20), the Gibbs equation for a mixture that is *always* in stable chemical equilibrium reduces to $TdS = dH - Vdp$ and we obtain the well know relation between thermodynamic temperature, enthalpy and entropy,

$$T = \left(\frac{\partial H}{\partial S}\right)_{p|E} \quad \text{(chemical equilibrium)} \tag{21}$$

C. Unstable chemical states

Due to a sufficiently large energy barrier, a reactable mixture might remain away from its stable chemical equilibrium state, while mechanically and thermally it is in equilibrium (homogeneous pressure and temperature). For instance, mixtures of hydrogen and oxygen are well known to remain unchanged until a spark induces the uncontrolled chain reaction in which they react to water. Although graphite is the stable from of carbon at standard temperature and pressure, diamonds, the unstable phase, "are forever".

For such unstable systems, one can control the composition of the mixture by a well designed technical apparatus. An example process for the H_2-O_2-H_2O reaction is as follows: (a) control temperature through a heat bath and pressure through the weight of a piston; (b) take a small portion of the mixture and use a membrane system to separate into the constituents (requires work); (c) let H_2 and O_2 react in a fuel cell to produce electrical work and water; (d) mix the resulting water back into the mixture (possibly with a membrane system to produce some work). With this, the mole numbers, temperature and pressure are individually controlled, and the system can, indeed, provide net work.

The inverse process extracts water from the mixture, utilizes an eletrolyzer to split the into hydrogen and oxygen, and feeds the product back into the mixture. The process must not be reversible, but as described it could even be idealized as a reversible process.

For systems that are in stable thermal and mechanical equilibrium, but not in stable chemical equilibrium, and for which the composition can be controlled, the law of mass action does *not* hold, i.e.,

$$\sum_\alpha \gamma_\alpha \mu_\alpha \neq 0 \quad \text{(chemical non-equilibrium)} \tag{22}$$

For a process at constant temperature and pressure, and varying composition, the Gibbs equation (19) reduces to

$$T\left(\frac{\partial S}{\partial \Lambda}\right)_{T,p} = \left(\frac{\partial H}{\partial \Lambda}\right)_{T,p} - \sum_\alpha \gamma_\alpha \mu_\alpha \; . \tag{23}$$

Entropy and enthalpy of the mixture change due to the change in composition. With $dn_\alpha = \gamma_\alpha d\Lambda$ and

$$H = \sum_\alpha n_\alpha h_\alpha \left(T, p, X_\alpha\right) \quad , \quad S = \sum_\alpha n_\alpha s_\alpha \left(T, p, X_\alpha\right) \; , \tag{24}$$

we find after careful calculation

$$\left(\frac{\partial H}{\partial \Lambda}\right)_{T,p} = \sum_\alpha \gamma_\alpha h_\alpha \quad , \quad \left(\frac{\partial S}{\partial \Lambda}\right)_{T,p} = \sum_\alpha \gamma_\alpha s_\alpha \; . \tag{25}$$

Hence, for this case (control of population in chemical non-equilibrium state) the Gibbs equation is fulfilled due to the definition of the chemical potential,

$$\mu_\alpha = h_\alpha - Ts_\alpha \quad \Rightarrow \quad T\sum_\alpha \gamma_\alpha s_\alpha = \sum_\alpha \gamma_\alpha h_\alpha - \sum_\alpha \gamma_\alpha \mu_\alpha \tag{26}$$

Most importantly, the variation of enthalpy and entropy due to change in composition cannot be used to find the temperature of the mixture:

$$\left(\frac{\partial H}{\partial S}\right)_{T,p} = \frac{\left(\frac{\partial H}{\partial \Lambda}\right)_{T,p} d\Lambda}{\left(\frac{\partial S}{\partial \Lambda}\right)_{T,p} d\Lambda} = \frac{\sum_\alpha \gamma_\alpha h_\alpha}{\sum_\alpha \gamma_\alpha s_\alpha} = \frac{\Delta h_R}{\Delta s_R} \neq T \; . \tag{27}$$

Here, Δh_R and Δs_R are the enthalpy and entropy of reaction (including mixing contributions). Note that for the hydrogen-oxygen reaction both have the same sign, so that $\frac{\Delta h_R}{\Delta s_R} > 0$, but there are reactions for which this ratio is negative, $\frac{\Delta h_R}{\Delta s_R} < 0$, such as the combustion of carbon, with the reaction $C + O_2 \rightleftharpoons CO_2$, or the phase change between graphite and diamond.

In the controlled process towards stable chemical equilibrium discussed above, enthalpy and entropy change, but their ratio $\frac{\partial H}{\partial S}$ is not the temperature T of the system. Indeed, the relation $T = \left(\frac{\partial H}{\partial S}\right)_X$ requires processes in which the system is in stable equilibrium states (chemical, mechanical and thermal) at all times. Work can be produced as the system approaches its stable equilibrium state, where the deviation from the stable equilibrium state serves as the driving force for the process.

D. Work from systems in chemical non-equilibrium

Next, we consider 1st and 2nd law for the controlled change of composition in chemically unstable systems. There are two work contributions, the volume change work $p\frac{dV}{dt}$ for the isobaric process, and the contribution $\dot{W}_c$ related to the chemical changes (e.g., fuel cell, electrolyzer). Heat will be exchanged with a reservoir at temperature T to keep the system temperature constant. Accordingly, 1st and 2nd law assume the form (enthalpy is $H = U + pV$)

$$\frac{dH}{dt} = \dot{Q} - \dot{W}_c \quad , \quad \frac{dS}{dt} - \frac{\dot{Q}}{T} = \dot{S}_{gen} \geq 0 \ . \tag{28}$$

Eliminating heat between the two laws, and use of the Gibbs equation (for fixed T, p) yields

$$\dot{W}_c = -\sum_\alpha \gamma_\alpha \mu_\alpha \frac{d\Lambda}{dt} - T\dot{S}_{gen} \lesseqgtr 0 \ . \tag{29}$$

There is no sign limitation for the reaction rate $\frac{d\Lambda}{dt}$, since the composition of the metastable state can be controlled in any direction. This control of composition is exclusively via work, not heat. In case of the hydrogen-oxygen-water system one would employ, e.g., electrolyzer and fuel cell. For a controlled phase change between diamond and graphite, one has to heat, compress or expand, and cool.

We consider both directions, charge and discharge of the system. To charge the system, the power is negative, $\dot{W}_c^c < 0$, work is done to the system, and stored in the nonequilibrium state. For discharge, the power is positive, $\dot{W}_c^d > 0$, and work is obtained from the system, which is released from the nonequilibrium state.

Typically one will expect irreversible losses within the process, which lead to work loss $T\dot{S}_{gen} > 0$, hence extra work is required for the charging process, and less work obtained from the discharge process. For a charge-discharge process that ends at the initial composition, the difference between stored and returned work (power integrated over the duration of the process) is the total work loss

$$W_{loss} = |W_c^c| - W_c^d = T\left(S_{gen}^d + S_{gen}^c\right) \geq 0 \ , \tag{30}$$

which is positive, as long as the thermodynamic temperature of the heat bath is positive.

For the example, work is required to split water into hydrogen and work can be obtained from the controlled reaction of hydrogen and oxygen. The driving force for the generation of work is the system's desire to reach the stable chemical equilibrium state, where almost all of the hydrogen has reacted (assuming sufficient amount of oxygen in the system).

III. A SIMPLE QUANTUM SYSTEM WITH APPARENT NEGATIVE TEMPERATURE

It is useful to have a simple system to study inverted states, for which, following Hoffmann [8], we consider a system of n quantum elements, that can assume only two states, at molar energies $\varepsilon_1 = 0$ and $\varepsilon_2 = \Delta\varepsilon$. The system is described as a mixture of two components, and system entropy is just the entropy of mixing of the two states, with molar entropies of the components $s_a = -R\ln X_a$; R is the universal gas constant.

A. Energy and entropy

The composition of the system is described through a single mole fraction $X = 1 - X_1 = X_2 = \frac{n_2}{n}$. Hence in this simple model, total energy and entropy of the system are

$$E = \sum_{a=1}^{2} n_a \varepsilon_a = n\Delta\varepsilon X \ , \tag{31}$$

$$S = \sum_{a=1}^{2} n_a s_a = -nR\left[(1-X)\ln(1-X) + X\ln X\right] \ , \tag{32}$$

This quantum system has a non-monotonous relation between energy and entropy with slope

$$\frac{dS}{dE} = \frac{\frac{dS}{dX}}{\frac{dE}{dX}} = \frac{R}{\Delta\varepsilon}\left(\ln\frac{1-X}{X}\right) \ , \tag{33}$$

which will be positive for $X < \frac{1}{2}$ and negative for $X > \frac{1}{2}$. Figure 4 shows the relation between molar energy, $e = E/n$ and molar entropy, $s = S/n$.

The thermodynamic description for this mixture is just as for the mixtures discussed above, when we chose the stoichiometric coefficients $\gamma_1 = -1$ and $\gamma_2 = 1$, and the reaction rate $\frac{d\Lambda}{dt} = n\frac{dX}{dt}$. The chemical potentials of the components are $\mu_a = \varepsilon_a - Ts_a$, and it is easy to verify that the Gibbs equation reads

$$TdS = dE - \sum_{a=1}^{2} \gamma_a \mu_a d\Lambda \ . \tag{34}$$

Here, T is the temperature of a heat bath, with which the quantum system is in thermal equilibrium.

B. Standard states

The stable equilibrium distribution of states is determined from the law of mass action (20),

$$\sum_{a=1}^{2}\gamma_a\mu_a = 0 \quad\Longrightarrow\quad X_{|E} = \frac{\exp\left[-\frac{\Delta\varepsilon}{RT}\right]}{1+\exp\left[-\frac{\Delta\varepsilon}{RT}\right]} \ . \tag{35}$$

We note that within classical thermodynamics the temperatures are positive, so that $X_{|E} < \frac{1}{2}$.

For the equilibrium state found above, the Gibbs equation (34) reduces to

$$TdS_{|E} = dE_{|E} \ , \tag{36}$$

and we find the classical equilibrium relation between entropy, energy and temperature as

$$\left(\frac{dS}{dE}\right)_{|E} = \frac{R}{\Delta\varepsilon}\left(\ln\frac{1-X_{|E}}{X_{|E}}\right) = \frac{1}{T} \ . \tag{37}$$

C. Inverted states

For inverted states, however, the law of mass action does not hold and (35) is not valid, therefore temperature T of the heat bath and distribution X of the quantum state are independent parameters. While the Gibbs equation (34) holds, it does not provide any additional information. The temperature of the heat bath T occurs in the Gibbs equation, but entropy and energy of the quantum system (31, 32) are *only determined through the quantum distribution X, and independent of temperature.*

With the law of mass action *not* fulfilled, one finds from the Gibbs equation (34)

$$\begin{aligned}\frac{dS}{dE} &= \frac{1}{T}\left(\frac{dE}{dE} - \sum_{\alpha}\gamma_a\mu_\alpha\frac{d\Lambda}{dE}\right)\\ &= \frac{1}{T}\left(\frac{T\left(s_2-s_1\right)}{\Delta\varepsilon}\right) = \frac{R}{\Delta\varepsilon}\left(\ln\frac{1-X}{X}\right) \ .\end{aligned} \tag{38}$$

This just is (33), while heat bath temperature T cancels out.

On first glance, the equation $\frac{dS}{dE} = \frac{R}{\Delta\varepsilon}\ln\frac{1-X}{X}$ appears to be the same as (37). However, in the present case, the ratio $\frac{dS}{dE}$ is not related to the temperature of a heat buth with which the quantum system is (or could be) in equilibrium. This result is parallel to our earlier finding in (27) for a metastable mixture, namely that in chemical non-equilibrium, the derivative $\frac{\partial H}{\partial S}$ is not the temperature of the system.

Reminding the reader that we describe all processes occurring within the framework of classical thermodynamics, where thermodynamic temperature is positive, we summarize as follows: For any $X < \frac{1}{2}$, i.e., for standard states, one can find a heat bath at thermodynamic temperature $T = \left[\frac{R}{\Delta\varepsilon}\left(\ln\frac{1-X_{|E}}{X_{|E}}\right)\right]^{-1} > 0$ such that the quantum system is in thermal equilibrium with the heat bath. For $X > \frac{1}{2}$, i.e., for inverted states, the quantum system is in a non-equilibrium state, and no heat bath exits, with which the system can be in thermal equilibrium.

D. Processes on the curve $E\left(S\right)$

If we allow the quantum system to exchange energy with a classical heat bath (reservoir) at positive temperature T_R, 1st and 2nd law assume their usual form,

$$\frac{dE}{dt} = \dot{Q} - \dot{W} \quad , \quad \frac{dS}{dt} - \frac{\dot{Q}}{T_R} = \dot{S}_{gen} \geq 0 \ , \tag{39}$$

where the system boundary is at the temperature of the heat bath.

We show the well-known result that states on the non-equilibrium branch of the curve $S(E)$, where $X > \frac{1}{2}$, cannot be reached along the curve $S(E)$, when the starting point is a stable state [9]. For this, the system energy E must be increased either by heating, or by work. For all processes on the curve, energy and entropy are given by (31, 32), that is entropy and energy are related by (33), and the two laws assume the form

$$\begin{aligned} n\Delta\varepsilon\frac{dX}{dt} &= \dot{Q} - \dot{W} \quad , \\ nR\left(\ln\frac{1-X}{X}\right)\frac{dX}{dt} - \frac{\dot{Q}}{T_R} &= \dot{S}_{gen} \geq 0 \ . \end{aligned} \tag{40}$$

For pure heat exchange between the system and the heat bath at temperature T_R, that is for $\dot{Q} \neq 0, \dot{W} = 0$, the laws can be combined to

$$n\Delta\varepsilon\left[\frac{R}{\Delta\varepsilon}\left(\ln\frac{1-X}{X}\right) - \frac{1}{T_R}\right]\frac{dX}{dt} = \dot{S}_{gen} \geq 0 \ . \tag{41}$$

This equation describes the irreversible approach to the stable equilibrium state of the combined system consisting of quantum system *and* heat bath. Driving force for the process is the temperature difference between quantum system and heat bath, and the process comes to an end in the final equilibrium state, when the system temperature equals the heat bath temperature,

$$\frac{R}{\Delta\varepsilon}\left(\ln\frac{1-X_{|E}}{X_{|E}}\right) = \frac{1}{T_R} \tag{42}$$

Since no (classical) heat bath can have a negative thermodynamic temperature, heating can at best bring the system to the maximum of the curve, where $X_{|E} = \frac{1}{2}$, and the temperature of heat bath and quantum system is $T = \infty$. For heat baths with finite temperature $0 < T_R < \infty$, we find $X_{|E} < \frac{1}{2}$.

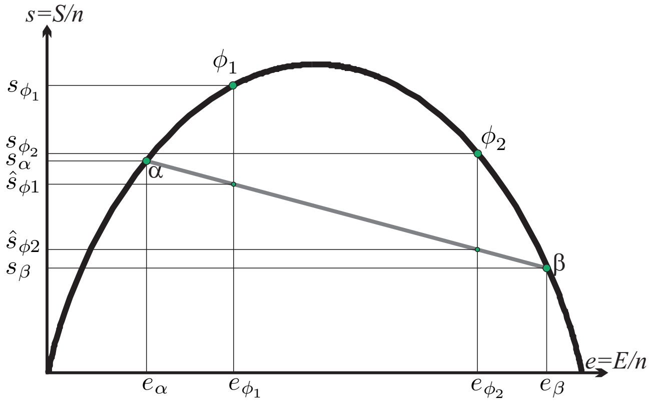

FIG. 4: Mixing of states in two invertible quantum systems. State α is on the stable branch, and state β is on the unstable branch. Mixed states ϕ_1 and ϕ_2 are stable and unstable, respectively.

For an adiabatic system, $\dot{Q} = 0$, the laws reduce to

$$n\Delta\varepsilon \frac{dX}{dt} = -\dot{W} \quad , \quad nR\left(\ln\frac{1-X}{X}\right)\frac{dX}{dt} = \dot{S}_{gen} \geq 0 \ . \tag{43}$$

While doing work to the system ($\dot{W} < 0$) increases energy, the 2nd law only allows X to grow (initially $X < \frac{1}{2}$!), and the process comes to a stop when $X = \frac{1}{2}$, which, again, corresponds to infinite temperature of the (thermally isolated) quantum system.

It follows that states on the descending branch ($X > \frac{1}{2}$) can only be reached by processes that leave the curve $S(E)$, as discussed in the main paper.

E. Two quantum systems in contact

We consider energy exchange between two quantum systems in standard and/or inverted states. E.g., consider two states with mole numbers n_α, n_β, energies

$$E_\alpha = n_\alpha e_\alpha = n_\alpha \Delta\varepsilon X_\alpha \quad , \quad E_\beta = n_\beta e_\beta = n_\beta \Delta\varepsilon X_\beta \tag{44}$$

and corresponding entropies

$$\begin{aligned} S_\alpha &= n_\alpha s_\alpha = -n_\alpha R\left[(1-X_\alpha)\ln(1-X_\alpha) + X_\alpha \ln X_\alpha\right] \\ S_\beta &= n_\beta s_\beta = -n_\beta R\left[(1-X_\beta)\ln(1-X_\beta) + X_\beta \ln X_\beta\right] \end{aligned} \tag{45}$$

The two systems are brought into contact, so that there is no work exchange with the surroundings, and the compound system is adiabatically shielded. The quantum elements interact, mixing their states, and the two laws of thermodynamics give for the final state (ϕ)

$$E_\phi = E_\alpha + E_\beta \quad , \quad S_\phi = S_\alpha + S_\beta + S_{gen} \tag{46}$$

so that

$$X_\phi = \frac{X_\alpha}{1+\frac{n_\beta}{n_\alpha}} + \frac{X_\beta}{\frac{n_\alpha}{n_\beta}+1} \tag{47}$$

We define the mole specific entropy of the two systems before interaction as

$$\hat{s}_\phi = \frac{S_\alpha + S_\beta}{n_\alpha + n_\beta} = \frac{s_\alpha}{1+\frac{n_\beta}{n_\alpha}} + \frac{s_\beta}{\frac{n_\alpha}{n_\beta}+1} \ . \tag{48}$$

Depending on the mole ratio $\frac{n_\alpha}{n_\beta}$, the curve $\{\hat{s}_{\alpha+\beta}, X_{\alpha+\beta}\}$ is a straight line connecting states α, β as shown in Fig. 4. Due to the concavity of the relation $S(E)$, it is clear that

$$\frac{S_{gen}}{n_\alpha + n_\beta} = \frac{S_\phi}{n_\alpha + n_\beta} - \frac{S_\alpha + S_\beta}{n_\alpha + n_\beta} = s_\phi - \hat{s}_{\alpha+\beta} > 0 \ . \tag{49}$$

The figure indicates mixing between a stable state α and an inverted state β. The final state depnds on the mole numbers n_α and n_β, and the figure indicates the stable mixing state ϕ_1 and the inverted mixing state ϕ_2.

We emphasize that this process is described as mixing and redistribution of energies between quantum systems. There is no need to consider heat transfer based on temperature difference between these systems.

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[10] The Kelvin-Planck Statement concerns heat drawn from the single reservoir–without a driving force–and fully converted to heat, while the Stability Statement concerns work produced from the reservoir directly. Kestin states that, without proof, that both statements are equivalent [6]. Here we see that they lead to the same conclusions.