2.43 ADVANCED THERMODYNAMICS

Spring Term 2024
LECTURE 02

Room 3-442
Friday, February 9, 11:00am - 1:00pm

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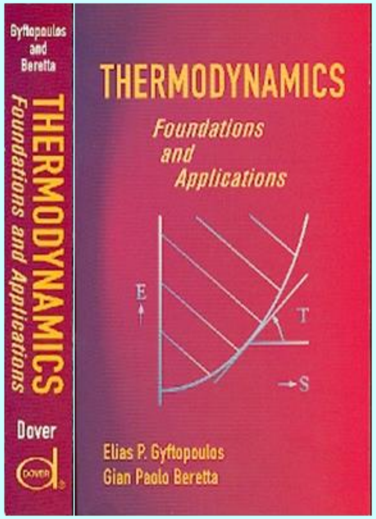
Room 3-351d

General course objective:

understand and learn to expose a consistent set of rigorous foundations of thermodynamics with emphasis on the assumptions used to model nonequilibrium and irreversible processes



Part I: concise review of basic concepts and definitions

Contents:

- Nonstandard statements of the First and the Second Law
- Rigorous definition of entropy valid for nonequilibrium
- Energy versus Entropy diagrams to illustrate basic results
- Rigorous definition of Heat Interaction
- Simple system model
- Bulk flow and local quasi-equilibrium models
- Exergy and second-law efficiency
- Allocation of consumptions and productions in hybrid power facilities

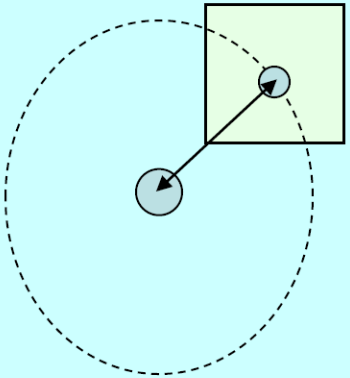
Review of basic concepts and definitions:

system
property
state
process

Review of basic concepts: The loaded meaning of the word SYSTEM

System: set of **constituents**, not subjected to forces that depend on coordinates of other external constituents, defined by:

- Type(s) and **amounts** of constituents
- **External forces** (between constituents of the system and external constituents), characterized by external **parameters** (e.g. *volume*)
- Internal forces (between constituents of the system)
- Internal partitions and constraints characterized by additional internal **parameters** and relations between paramaters



- The force between electron and nucleus depends on their relative distance

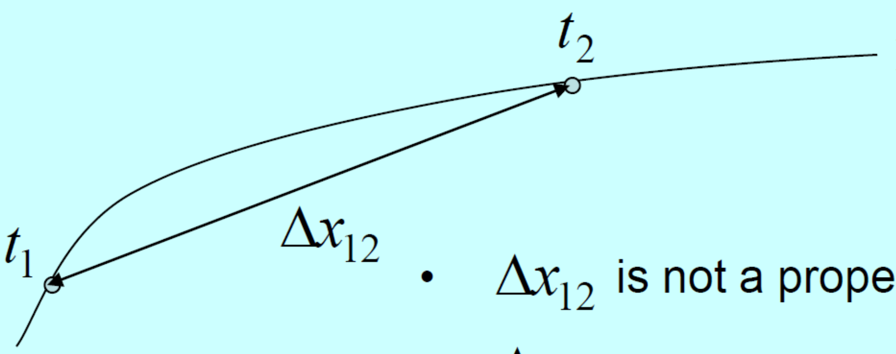
⇒ The electron by itself cannot qualify as a *system*

Environment of a system: the rest of the Universe (or the part of it which is relevant for the purposes of the model)

Review of basic concepts: The loaded meaning of the word PROPERTY

Property: defined by a measurement procedure which, when applied to the system at time *t*, yields a numerical result *P(t)*, which **must not depend on other instants of time**, and be independent of

- Different measuring apparati which apply the same procedure
- Different environmental conditions



Example: path of a material point

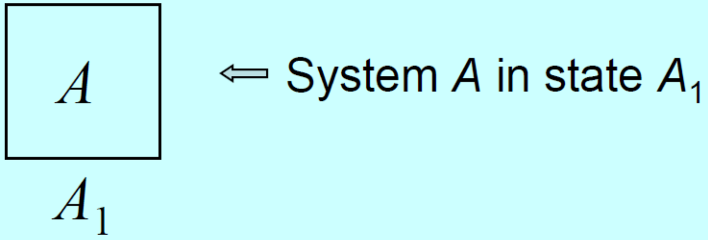
- Δx_{12} is not a property (it depends on both t_1 and t_2)
- $\dfrac{\Delta x_{12}}{t_2 - t_1}$ is not a property (it depends on both t_1 and t_2)
- $w_1 = \lim\limits_{t_2 \to t_1} \dfrac{\Delta x_{12}}{t_2 - t_1}$ is a property (it depends on t_1 only)

Review of basic concepts: What exactly do we mean by the word STATE (of a system)

State: the state of the system at time *t* is the set of (a) the values of the amounts of all constituents, (b) the values of the external and internal, and (c) the values of all the conceivable properties

$$A(t)=\{n_1(t),\ldots,n_r(t),\beta_1(t),\ldots,\beta_s(t),P_1(t),P_2(t),\ldots\}$$

r = number of different constituents
s = number of parameters



⇐ System A in state A_1

<u>Time evolution of the state of the system:</u>

The state of the system can evolve

- Spontaneously (due to its internal dynamics, internal redistributions)
- As a result of interactions with other systems in its environment

Isolated system: a system which cannot be affected by its environment, and conversely which cannot cause any change of state of the environment.

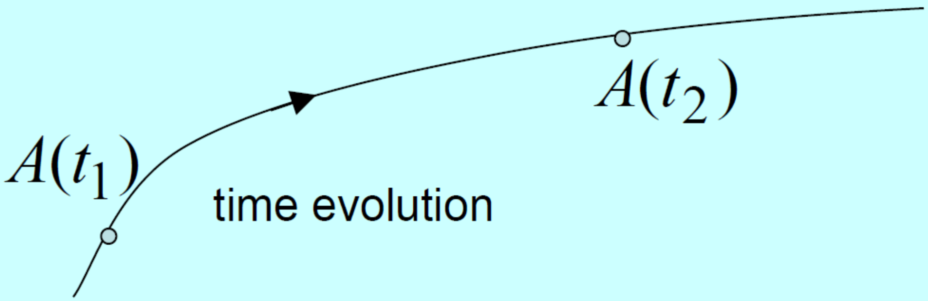
Review of basic concepts: What do we mean by general LAWS of time evolution

State: the state of the system at time *t* is the set of (a) the values of the amounts of all constituents, (b) the values of the external and internal, and (c) the values of all the conceivable properties

$$A(t)=\{n_1(t),\ldots,n_r(t),\beta_1(t),\ldots,\beta_s(t),P_1(t),P_2(t),\ldots\}$$

General equation of motion:

$$\frac{dA(t)}{dt}=f\left[A(t),\text{forces}(t)\right]\rightarrow$$



Two theorems of the equation of motion hold **for all (well-defined) systems**:

1. First theorem
2. Second theorem

Historically discovered before the general equation of motion, they are **postulated** as:

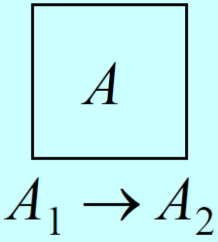
1. **First law** of T.
2. **Second law** of T.

To be acceptable, a general equation of motion must imply them as theorems.

Review of basic concepts: Time evolution, interactions, and the concept of PROCESS

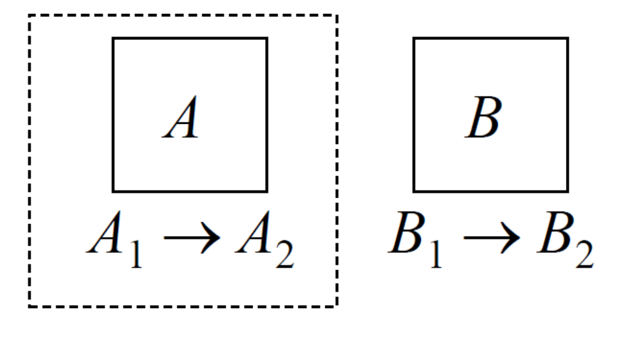
Process: it is specified by

- The initial state of the system
- The final state of the system
- The effects produced by the interactions with other systems (in practice, the change of state of the environment)



⇐ System *A* undergoing a process from state A_1 to state A_2

To define a process we must describe also the effects on the environment *B* of system *A* ⟹

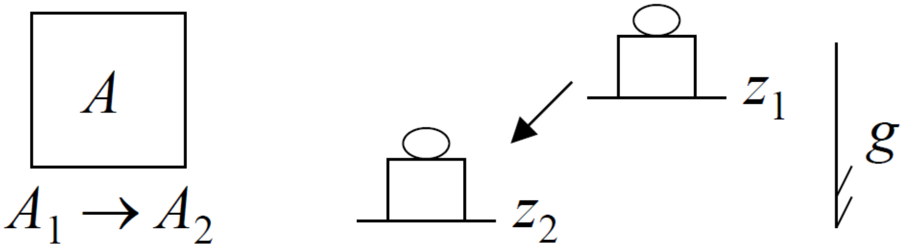


Review of basic concepts: **definition of** WEIGHT PROCESS

Processes can be classified…

… on the basis of the effects they produce in the environment:

- ***Spontaneous Process*** (no effects on the environment)
- ***Weight Process*** (external effects are only “mechanical”, such as the change in elevation of a weight)



The only effect external to *A*

Note1 = A system is isolated if it can only undergo spontaneous processes.
Note2 = A spontaneous process is a weight process with no change in elevation of the weight

Review of basic concepts:

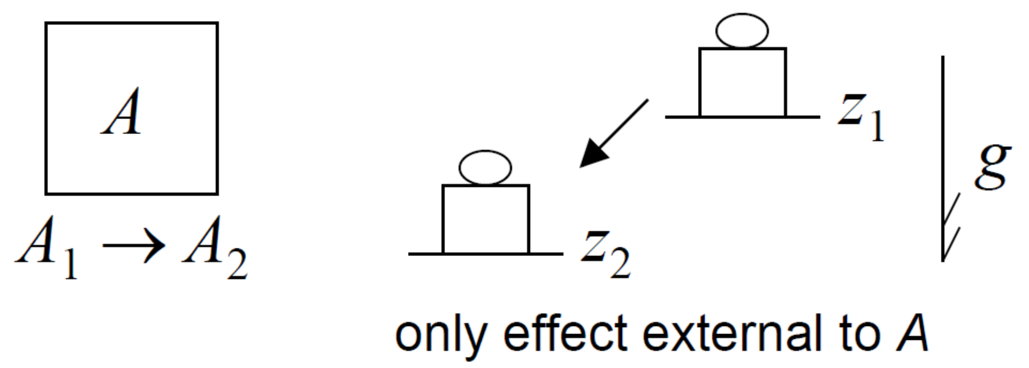
First Law,
definition of Energy,
Energy balance

Review of basic concepts: Main consequence of the First Law: definition of property Energy

First Law:

Assertion 1: any pair of states A_1 and A_2 with compatible values of the amounts of constituents and the parameters of a (well-defined) system A can always be interconnected by means of a weight process.

Assertion 2: the product $mg\,(z_2 - z_1)$ assumes the same value for all weight processes that connect the two given states A_1 and A_2.



The most important consequence of the First Law is that it provides support to the **definition of property energy** for every (well-defined) system *A* in any state A_1

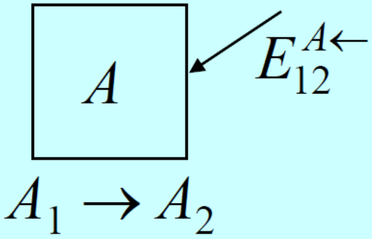
$$E_1^A = E_0^A - mg(z_1 - z_0)$$

where A_0 is a reference state to which we assign the arbitrary value E_0.

Review of basic concepts: Consequences of the First Law:

Energy balance equation

Energy balance equation for a process for system *A*:

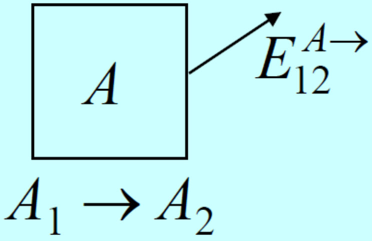


$$E_2^A - E_1^A = E_{12}^{A\leftarrow}$$

- $E_{12}^{A\leftarrow}$ energy exchanged between *A* and its environment during the time interval from t_1 to t_2 (if positive, the net transfer is into *A*)

or, equivalently,

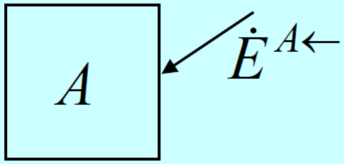
$$E_{12}^{A\leftarrow}$$



$$E_2^A - E_1^A = -E_{12}^{A\rightarrow}$$

- $E_{12}^{A\rightarrow}$ energy exchanged between *A* and its environment during the time interval from t_1 to t_2 (if positive, the net transfer is out of *A*)

For a continuous process, consider an infinitesimal time interval (t_1=t and t_2=t+dt)



$$\frac{dE^A}{dt} = \dot{E}^{A\leftarrow}$$

- $\dot{E}^{A\leftarrow}$ net power, net rate of energy transfer (into *A* if positive, out of *A* if negative)

Review of basic concepts:

Stable equilibrium states,
Reversible process,

Second Law,
Impossibility of PMM2,
Adiabatic Availability

Review of basic concepts: States can be Steady/Unsteady or Equilibrium/Nonequilibrium

States can be classified on the basis of:

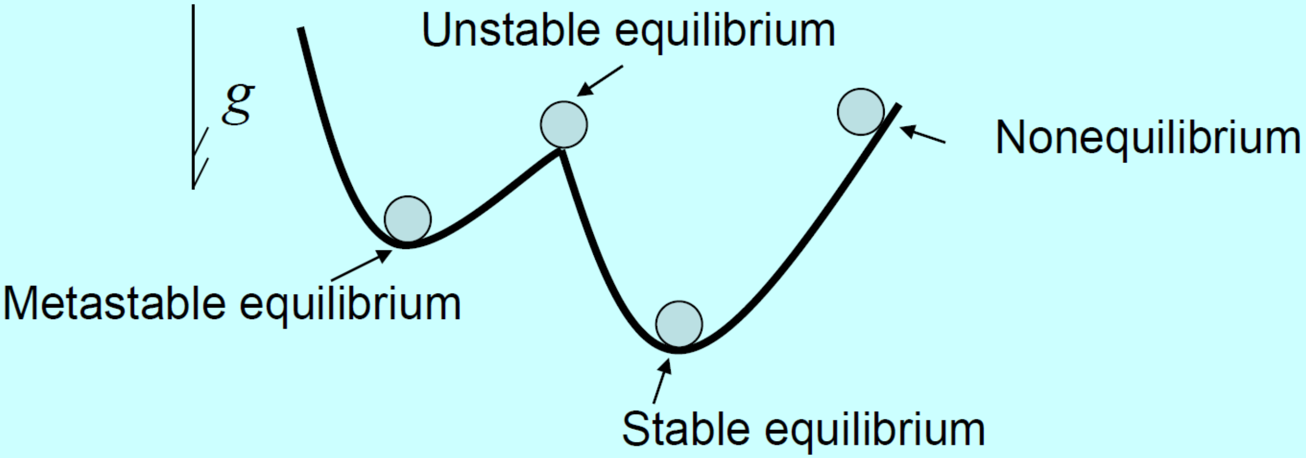
- *whether they change or not as a function of time*
- *whether such time behavior is due or not to interactions with other systems*

	…because of external interactions	…even if external interactions are turned off
The state changes with time…	Unsteady state	Nonequilibrium state
The state does not change with time…	Steady state	Equilibrium state

Review of basic concepts: Equilibrium states can be Unstable/Metastable/Stable

An equilibrium state is:

- ***Unstable***, if it can be changed to a different state by means of a process which produces an ***infinitesimal*** temporary external effect, but no net permanent external effect
- ***Metastable***, if it can be changed to a different state by means of a process which produces a ***finite*** temporary external effect, but no net permanent external effect
- ***Stable***, if it cannot be changed to a different state by means of any process which produces no net permanent external effect



Review of basic concepts: Hatsopoulos-Keenan statement of the Second Law of Thermodynamics

Addresses the question:

Among all the states of a system that have the same values of the amounts of constituents n and the parameters β of the external forces, how many are the stable equilibrium states?

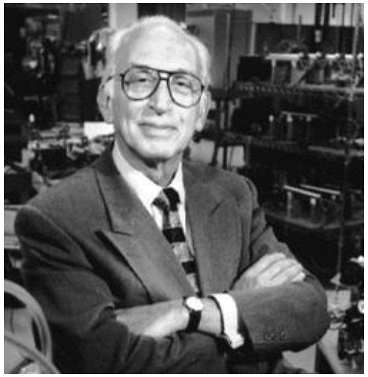
Answer in the domain of Mechanics:

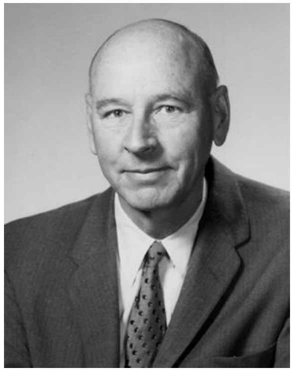
One and only one: the state with minimum energy, $E_g(n,\beta)$

Second Law:

Assertion 1: in the subset of states of a system compatible with given values of the amounts of constituents $\boldsymbol{n}$ and of the parameters $\boldsymbol{\beta}$, there is always one and only one SES for each value of the energy E.

Assertion 2: Starting from any state of the system, it is always possible, through a reversible weight process, to reach a SES with arbitrarily fixed, compatible values of the amounts of constituents and the parameters.





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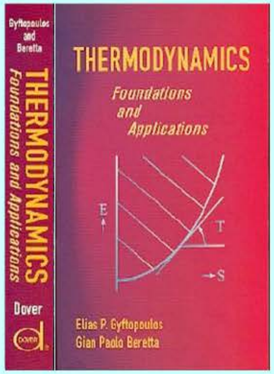
Answer in the domain of Thermodynamics:

One for every value of the energy E

This apparent contradiction is rationalized only when we realize that the domain of states contemplated by Thermodynamics is broader than that of Mechanics, and contains it.

Review of basic concepts: First Law and Second Law together entail many consequences

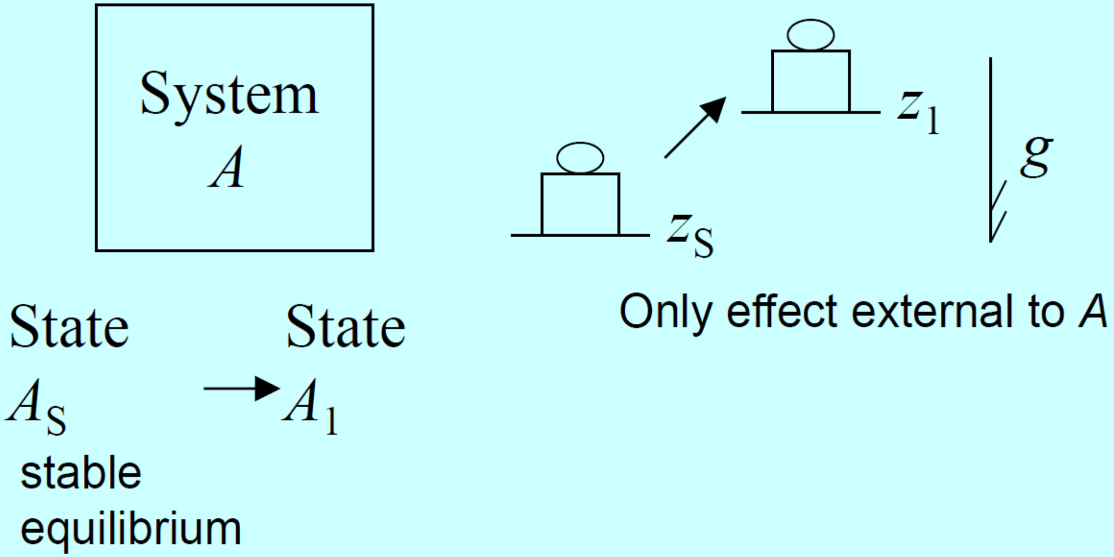
- ***Kelvin-Planck statement***: impossibility of perpetual motion of the second kind.
- Supports the definition of property **adiabatic availability**.
- Supports the definition of property **temperature of a thermal reservoir**.
- Supports the definition of property ***entropy.***
- Principle of nondecrease of entropy. Entropy balance.
- Criteria to determine if a process is reversible or not.
- State principle and fundamental relation for the stable equilibrium states.
- Conditions for mutual equilibrium between systems.
- **Clausius statement**: Conditions for the spontaneous exchange of energy between systems initially in stable equilibrium states but not in mutual equilibrium.
- Et cetera, see Gyftopoulos and Beretta, *Thermodynamics. Foundations and Applications*, Dover 2005 (or first edition, Macmillan 1991)



Review of basic concepts: Consequences of First&Second Law:

Theorem: Kelvin-Planck statement of the Second Law

PMM2: perpetual motion machine of the second kind



System A

State A_S stable equilibrium $\rightarrow$ State A_1

Only effect external to A

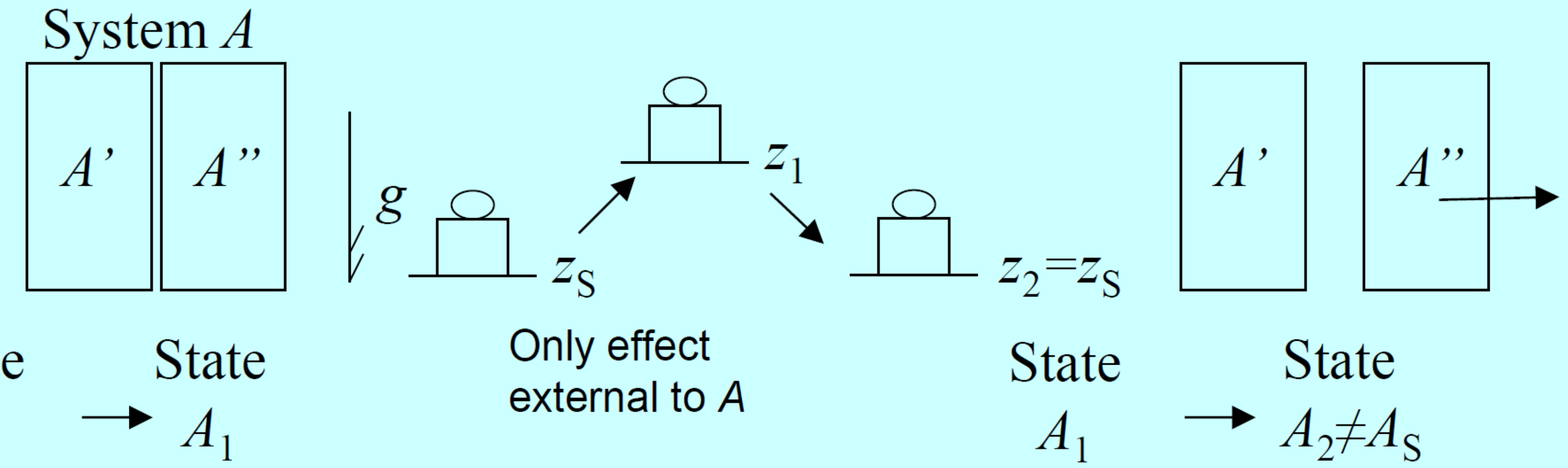
Theorem. It is impossible to extract mechanical energy without other effects from a system initially in a stable equilibrium state.

(Valid for all systems with translational, rotational and vibrational degrees of freedom, that from any state can receive energy by means of a weight process)

Review of basic concepts: Consequences of First&Second Law:

Proof of the Kelvin-Planck statement of the Second Law

Ab absurdo, assume that a perpetual motion machine of the second kind be possible
(further assume, for simplicity of proof here, that system A is composed of two separate parts)



State A_S stable equilibrium → State A_1

Only effect external to *A*

State A_1 → State $A_2 \neq A_S$

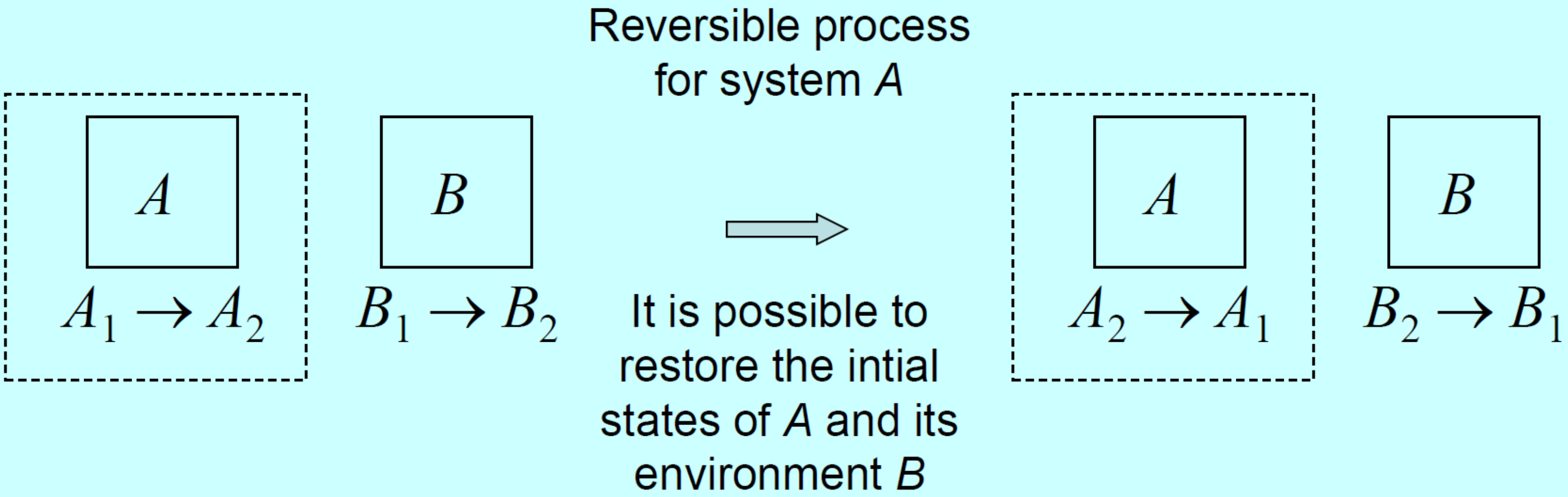
What does this violate?

Review of basic concepts: What exactly do we mean by REVERSIBLE PROCESS

Processes can be classified…

… on the basis of the possibility of “undoing” their effects:

- ***Reversible*** if all effects (including those external to the system) can be undone
- ***Irreversible*** if it is not reversible



Reversible process for system *A*

It is possible to restore the intial states of *A* and its environment *B*

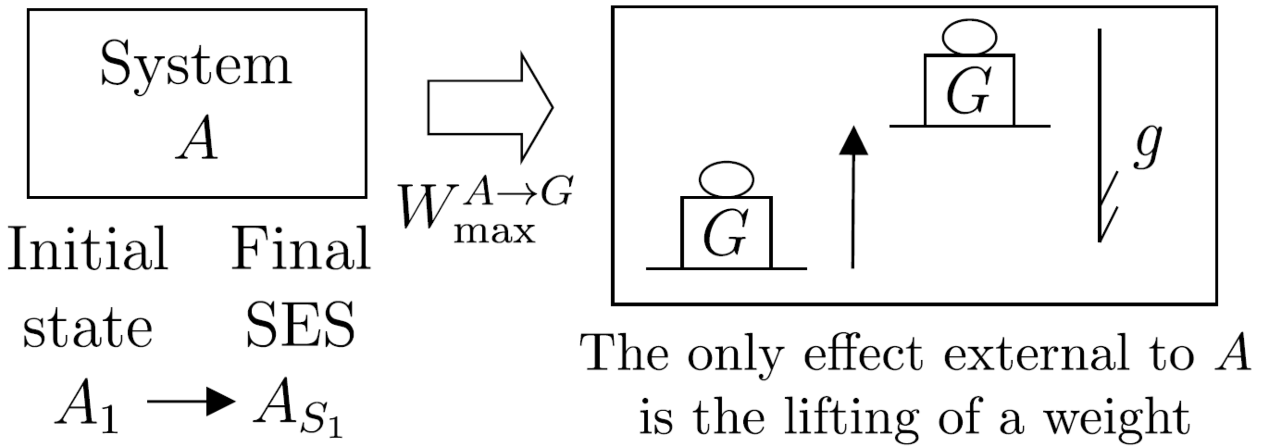
Review of basic concepts: **importance of the second part of the statement of the Second Law of Thermodynamics**

Second Law:

Assertion 1: in the subset of states of a system compatible with given values of the amounts of constituents $\boldsymbol{n}$ and of the parameters $\boldsymbol{\beta}$, there is always one and only one SES for each value of the energy E.

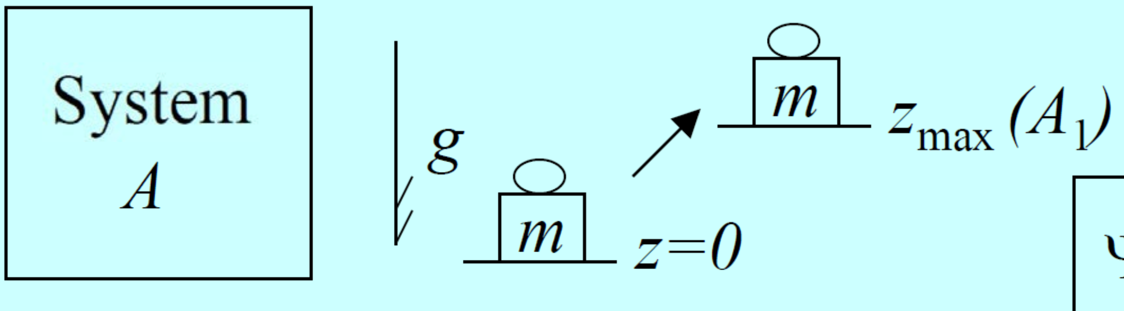
Assertion 2: Starting from any state of the system, it is always possible, through a reversible weight process, to reach a SES with arbitrarily fixed, compatible values of the amounts of constituents and the parameters.

Reversible weight process for A ending in a SES



The only effect external to A is the lifting of a weight

Review of basic concepts: Consequences of First&Second Law: definition of property Adiabatic Availability



$$\boxed{\Psi_1 = m g z_{\max}}$$

$$\text{State } A_1 \longrightarrow \text{State } A_{S1}$$

Only effect external to *A*

The **adiabatic availability** $\Psi^R{}_1$ of system *A* in state A_1 measures the maximum amount of energy that can be transferred from the system to a weight in a weight process for *A* starting from state A_1.

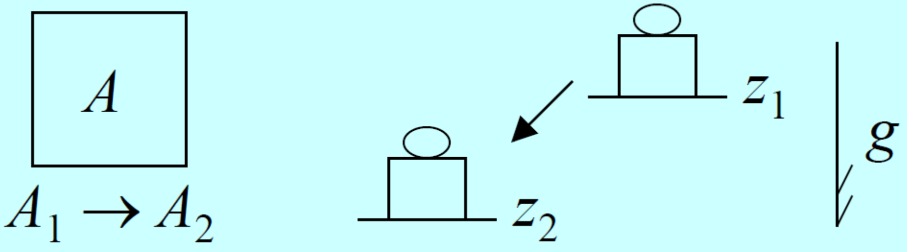
Theorems: Adiabatic availability is a property, but it is NOT additive.

From the energy balance we obtain $\boxed{\Psi_1 = E_1 - E_{S1}}$

It is zero if and only if the state is stable equilibrium.
It obtains when the weight process is reversible and *A* ends in stable equilibrium.
A unique stable equilibrium state A_{S1} can be reached in this way from state A_1.

Review of basic concepts: Consequences of the (First&)Second Law:

Theorem: criterion for the reversibility of a weight process



Theorem. The following equivalent conditions are necessary and sufficient for a weight process for system *A* to be reversible or irreversible:

reversibile iff:	**irreversible** iff:	impossible iff:
$E_2 - \Psi_2 = E_1 - \Psi_1$	$E_2 - \Psi_2 > E_1 - \Psi_1$	$E_2 - \Psi_2 < E_1 - \Psi_1$

see detailed proof at pag. 76 of the book

Review of basic concepts:

Mutual stable equilibrium,
Thermal reservoir,
definition of Temperature of a thermal reservoir,
definition of Entropy,
Available energy with respect to a thermal reservoir,
Entropy (in)balance,
Criteria for reversibility of a weight process

Review of basic concepts: Mutual equilibrium and definition of Thermal Reservoir

Mutual stable equilibrium: Two systems *A* and *B* are in mutual stable equilibrium if their respective states are such that the composite system *C*=*AB* is in a stable equilbrium state.

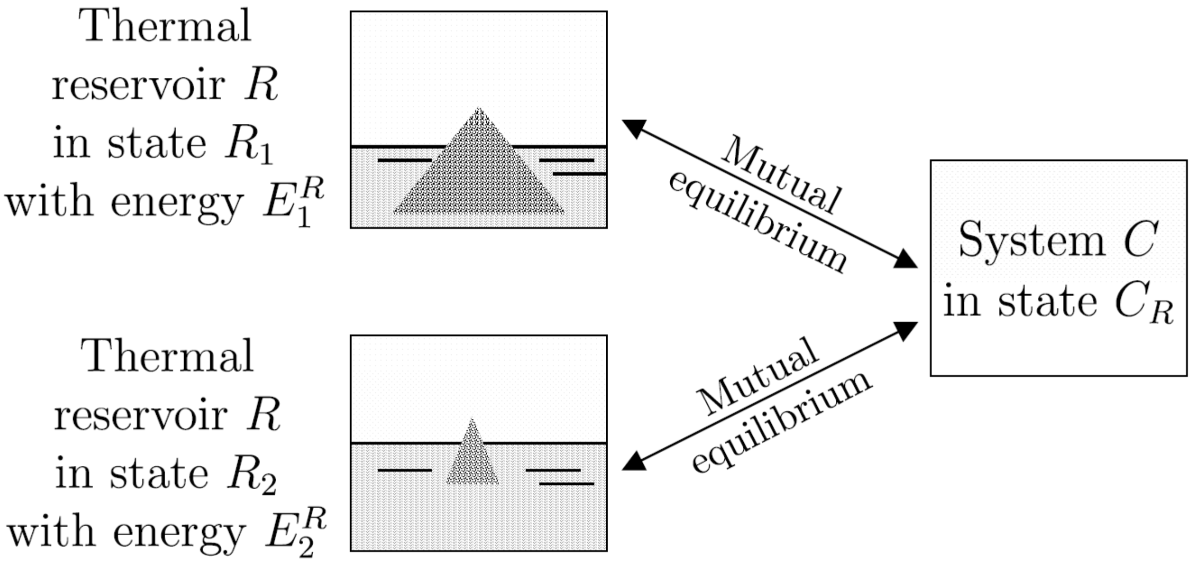
Thermal Reservoir (with constant amounts and parameters)**:** a system *R* that in any of its stable equilibrium states is in mutual equilibrium with a given system *C* in a given state C_R

Example of a reservoir:

- H_2O *at the triple point*

$$T_{pt} = 273.16\,\mathrm{K} \quad p_{pt} = 611.66\,\mathrm{Pa}$$

as long as all the three phases are present in a finite amount



Thermal reservoir R in state R_1 with energy E_1^R

Mutual equilibrium

System C in state C_R

Mutual equilibrium

Thermal reservoir R in state R_2 with energy E_2^R

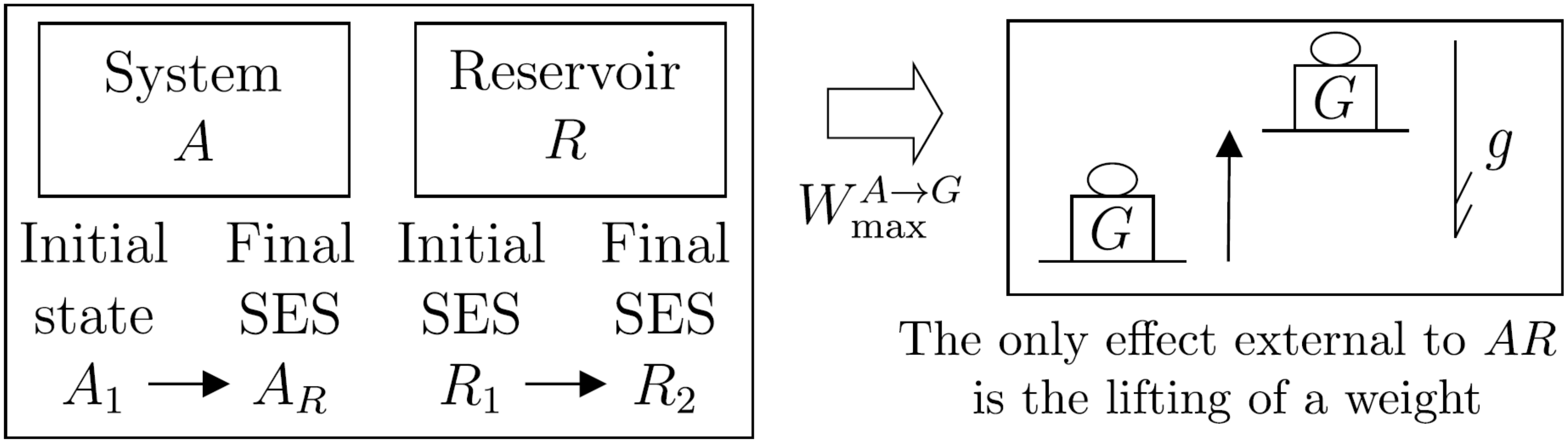
Review of basic concepts: importance of the second part of the statement of the Second Law of Thermodynamics

Second Law:

Assertion 1: in the subset of states of a system compatible with given values of the amounts of constituents $\boldsymbol{n}$ and of the parameters $\boldsymbol{\beta}$, there is always one and only one SES for each value of the energy E.

Assertion 2: Starting from any state of the system, it is always possible, through a reversible weight process, to reach a SES with arbitrarily fixed, compatible values of the amounts of constituents and the parameters.

Reversible weight process for AR ending with A and R in MSE

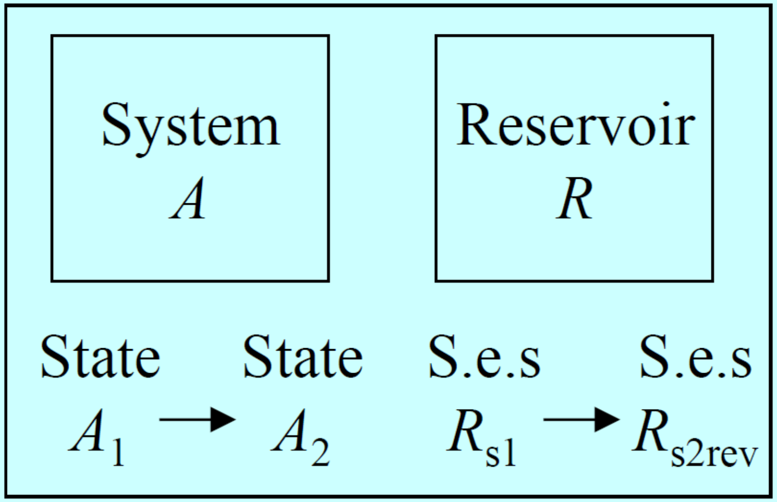


The only effect external to AR is the lifting of a weight

Review of basic concepts: **Consequences of the (First&)Second Law:**

Feasibility for arbitrary A, A_1, A_2, R, R_{s1} of the following

Standard reversible weight process for *AR*

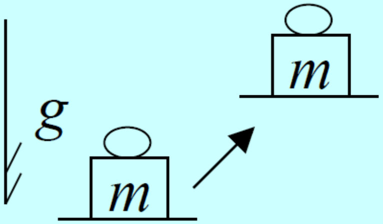


System A

Reservoir R

State A_1 → State A_2

S.e.s R_{s1} → S.e.s R_{s2rev}



This is the only effect external to *AR*.

Our statement of the Second Law warrants the feasibility of such process for arbitrary states A_1 and A_2 and any initial s.e.s. R_{s1} (these determine uniquely the final state R_{s2rev}).

We are interested in measuring the change in energy of the reservoir in this process, that we denote by

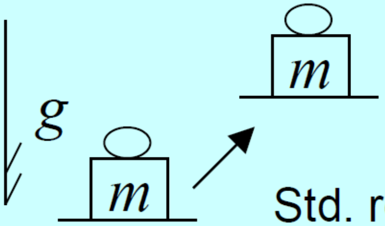
$$(E^R_{\mathrm{s2rev}} - E^R_{\mathrm{s1}})_{A_1 R_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R_{\mathrm{s2rev}}}$$

Review of basic concepts: Consequences of the (First&)Second Law: Measurement procedure defining the “constant temperature of a thermal reservoir”

System
A
auxiliary to this measure

Reservoir
R
the object of this measure

State	State	S.e.s	S.e.s
$A_1 \rightarrow$	A_2	$R_{s1} \rightarrow$	R_{s2rev}



Std. rev. w.p. for *AR*
Measure the change in E^R

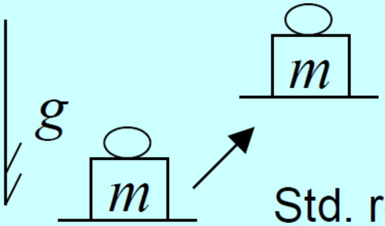
$$\frac{\left(E^R_{s2rev} - E^R_{s1}\right)_{A_1 R_{s1} \underset{w,rev}{\Rightarrow} A_2 R_{s2rev}}}{\left(E^{R^o}_{s2rev} - E^{R^o}_{s1}\right)_{A_1 R^o_{s1} \underset{w,rev}{\Rightarrow} A_2 R^o_{s2rev}}}$$

Repeat for the same A_1 and A_2, but with a reference reservoir R^0 *(water at the triple point)*

System
A
the same as above

Reference reservoir
$\boldsymbol{R^0}$

State	State	S.e.s	S.e.s.
$A_1 \rightarrow$	A_2	$R^o_{s1} \rightarrow$	R^o_{s2rev}



Std. rev. w.p. for AR^o
Measure the change in E^R

Review of basic concepts: Consequences of the (First&)Second Law:

Measurement procedure defining the “constant temperature of a thermal reservoir”

It can be proved that the ratio:

$$\frac{\left(E^{R}_{\mathrm{s2rev}} - E^{R}_{\mathrm{s1}}\right)_{A_1 R_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R_{\mathrm{s2rev}}}}{\left(E^{R^o}_{\mathrm{s2rev}} - E^{R^o}_{\mathrm{s1}}\right)_{A_1 R^o_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R^o_{\mathrm{s2rev}}}}$$

- is positive
- is independent of the initial states R_{s1} , R^0_{s1} of the reservoirs
- is independent of the choice of the auxiliary system A and of its states A_1 and A_2
- it depends therefore only on the pair of reservoirs R and R^0
- for a reference R^0 fixed once and for all, it is a *constant* property of reservoir R

  (it has the same value in all the stable equilibrium states of R)
- being a dimensionless number that emerges from the comparison with a reference reservoir, this property defines a new dimension and requires the choice of a new unit of measure
- this defines the property **temperature of reservoir** R:

$$T_R = T_{R^o}\,\frac{\left(E^{R}_{\mathrm{s2rev}} - E^{R}_{\mathrm{s1}}\right)_{A_1 R_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R_{\mathrm{s2rev}}}}{\left(E^{R^o}_{\mathrm{s2rev}} - E^{R^o}_{\mathrm{s1}}\right)_{A_1 R^o_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R^o_{\mathrm{s2rev}}}}$$

For R^0 chosen to be water at the triple point, we obtain the S.I. unit, the **kelvin**, defined by

$$T_{R^0} = 273.16\ \mathrm{K}$$

Review of basic concepts: Consequences of the (First&)Second Law: Measurement procedure defining the "constant temperature of a thermal reservoir"

Notice that from

$$T_R = T_{R^o} \frac{(E^R_{\mathrm{s2rev}} - E^R_{\mathrm{s1}})_{A_1 R_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R_{\mathrm{s2rev}}}}{(E^{R^o}_{\mathrm{s2rev}} - E^{R^o}_{\mathrm{s1}})_{A_1 R^o_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R^o_{\mathrm{s2rev}}}}$$

it follows that the ratio

$$\frac{(E^R_{\mathrm{s2rev}} - E^R_{\mathrm{s1}})_{A_1 R_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R_{\mathrm{s2rev}}}}{T_R} = \frac{(E^{R^o}_{\mathrm{s2rev}} - E^{R^o}_{\mathrm{s1}})_{A_1 R^o_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R^o_{\mathrm{s2rev}}}}{T_{R^o}}$$

- is independent of reservoir R and of its initial state R_{s1}
- It depends therefore only on system A and the pair of states A_1 and A_2

This observation prompts the following definition for the entropy difference between the states A_1 and A_2 of system A.

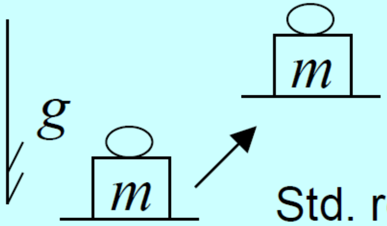
Review of basic concepts: **Consequences of the (First&)Second Law: definition of property Entropy**

System
A
the object of this measure

Reservoir
$\boldsymbol{R}$
auxiliary to this measure

State A_1 $\longrightarrow$ State A_0

S.e.s R_{s1} $\longrightarrow$ S.e.s R_{s0rev}



Std. rev. w.p. for *AR*
Measure the change in E^R

state A_0 is an arbitrarily chosen state to which we assign the arbitrary reference value S_0

The ratio:

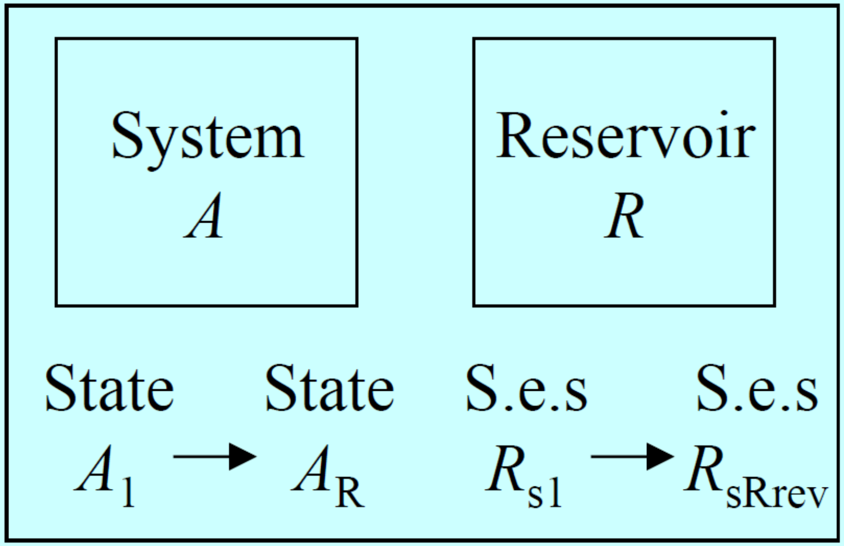
$$\frac{(E^R_{\mathrm{s0rev}} - E^R_{\mathrm{s1}})_{A_1R_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_0R_{\mathrm{s0rev}}}}{T_R}$$

- is independent of reservoir *R* and of its initial state R_{s1}
- It depends therefore only on system A and the pair of states A_1 and A_0

Hence it defines a property:

$$S_1 = S_0 + \frac{(E^R_{\mathrm{s0rev}} - E^R_{\mathrm{s1}})_{A_1R_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_0R_{\mathrm{s0rev}}}}{T_R}$$

Review of basic concepts: Consequences of the (First&)Second Law: definition of Available Energy w.r.to a thermal reservoir



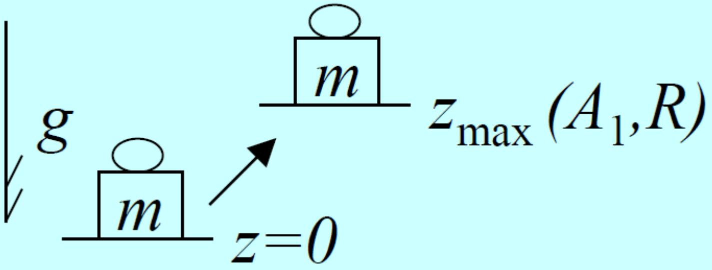
System A

Reservoir R

State A_1 → State A_R

S.e.s $R_{\mathrm{s}1}$ → S.e.s R_{sRrev}

Max weight lift in a std. w.p. for *AR*:



Given state A_1 and the reservoir *R*, the ***maximum weight lift*** obtains when *A* ends in state A_R (mutual equilibrium with *R*) and the standard weight process for *AR* is reversible.

We denote the energy transferred to the weight by

from the energy balance

$$\Omega_1^R = mgz_{\max} = (E_1 - E_\mathrm{R}) + (E_{\mathrm{s}1}^R - E_{\mathrm{sRrev}}^R)$$

and we call it the ***available energy*** of *A* in state A_1 ***with respect to reservoir*** *R*. From the definition of entropy, chosing state A_R as the reference state A_0,

$$S_1 = S_\mathrm{R} + \frac{E_{\mathrm{sRrev}}^R - E_{\mathrm{s}1}^R}{T_R} \longrightarrow \Omega_1^R = (E_1 - E_\mathrm{R}) - T_R(S_1 - S_\mathrm{R})$$

Review of basic concepts: Consequences of the (First&)Second Law: engineering meaning of Entropy

From the relation

$$\Omega_1^R = (E_1 - E_R) - T_R(S_1 - S_R)$$

We obtain the following interpretation of the physical meaning of entropy:

Energy of system A which is unavailable w.r.to reservoir *R* *(it cannot be given to a weight without other effects)*

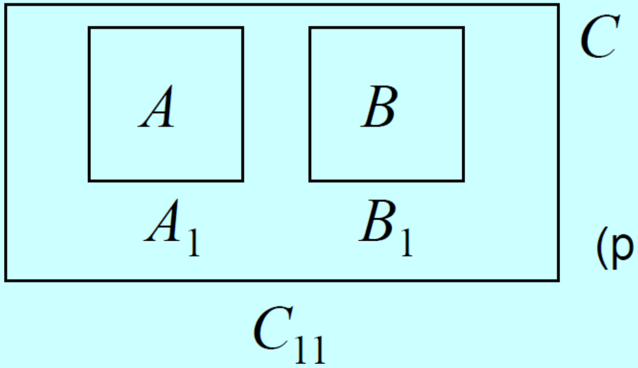
$$S_1 = \frac{E_1 - \Omega_1^R}{T_R} + S_R - \frac{E_R}{T_R}$$

A constant, independent of the state A_1

So, the entropy is a linear function of that part of the energy of the system which is unavailable with respect to reservoir, the constant of proportionality being the inverse of the temperature of the reservoir.

Review of basic concepts: Consequences of the (First&)Second Law: additivity of Entropy and impossibility of Entropy decrease in a weight process

Additivity of entropy: given two systems *A* and *B* and the *composite system* *C=AB*, for every state



$$S_{11}^C = S_1^A + S_1^B$$

(provided we choose $S_{00}^C = S_0^A + S_0^B$)

Principle of entropy non-decrease in weight processes: it fixed the direction in which a weight process between two states is possible

$$S_2 \geq S_1$$

= if the w.p. is reversible
> if the w.p. is irreversible

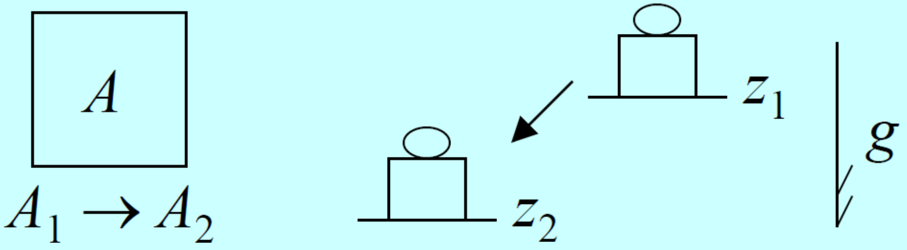
or, equivalently,

$$S_2 - S_1 = (S_{\text{irr}})_{12}$$

$(S_{\text{irr}})_{12} = 0$ if the w.p. is reversible
$(S_{\text{irr}})_{12} > 0$ if the w.p. is irreversible

Review of basic concepts: Consequences of the (First&)Second Law:

Criteria for the reversibility of a weight process

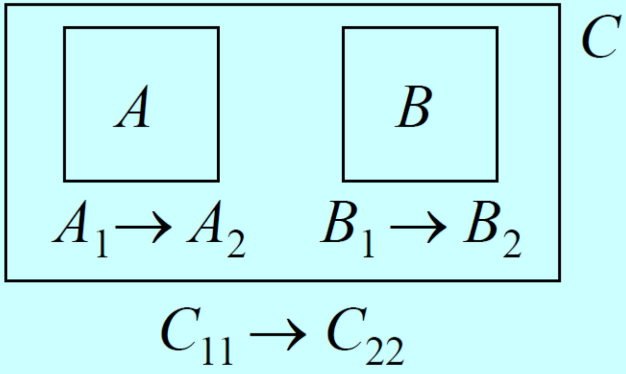


Theorem. The following equivalent conditions are necessary and sufficient for a <u>weight process</u> for system *A* to be reversible or irreversible:

reversibile iff:	**irreversible** iff:	impossible iff:
$E_2 - \Psi_2 = E_1 - \Psi_1$	$E_2 - \Psi_2 > E_1 - \Psi_1$	$E_2 - \Psi_2 < E_1 - \Psi_1$
$E_2 - \Omega_2^R = E_1 - \Omega_1^R$	$E_2 - \Omega_2^R > E_1 - \Omega_1^R$	$E_2 - \Omega_2^R < E_1 - \Omega_1^R$
$S_2 = S_1$	$S_2 > S_1$	$S_2 < S_1$

Review of basic concepts: Consequences of the (First&)Second Law: exchangeability of Entropy via interactions

Exchangeability of entropy: consider a reversible process for an isolated composite system *C*=*AB* in which *A* changes from A_1 to A_2 and *B* from B_1 to B_2



$$S_{22}^C = S_{11}^C$$

additivity $\Downarrow$

$$S_2^A + S_2^B = S_1^A + S_1^B$$

$$\Downarrow$$

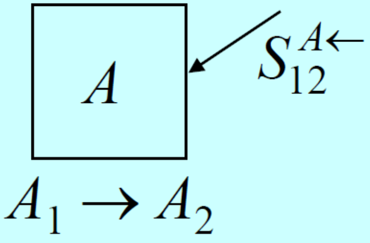
$$S_2^A - S_1^A = -(S_2^B - S_1^B)$$

- If the entropy of *B* has decreased, the entropy of *A* has increased by an equal amount, therefore, we can say that entropy has been transferred from *B* to *A*
- $S_{12}^{A\leftarrow B} = -(S_2^B - S_1^B)$, if positive, denotes the entropy that *A* received from *B*,
- otherwise, $-S_{12}^{A\leftarrow B} = S_{12}^{A\rightarrow B}$, if positive, denotes the entropy that *A* gives to *B*

Review of basic concepts: **Consequences of the (First&)Second Law:** Entropy balance equation

Entropy balance equation for a process for system *A*:

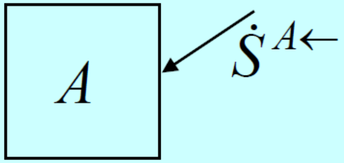
$$S_2^A - S_1^A = S_{12}^{A\leftarrow} + \left(S_{\text{irr}}\right)_{12}^A$$



- $S_{12}^{A\leftarrow}$ entropy exchanged between *A* and its environment during the time interval from t_1 to t_2 (if positive, the net transfer is into *A*)
- $\left(S_{\text{irr}}\right)_{12}^A \geq 0$ entropy generated by irreversibility within the system during the process (=0 if reversibile)

For a continuous process, consider an infinitesimal time interval (t_1=t and t_2=t+dt)

$$\frac{dS^A}{dt} = \dot{S}^{A\leftarrow} + \left(\dot{S}_{\text{irr}}\right)^A$$



- $\dot{S}^{A\leftarrow}$ net rate of entropy transfer (into *A* if positive, out of *A* if negative)
- $\left(\dot{S}_{\text{irr}}\right)^A \geq 0$ rate of entropy generation by irreversibility within the system (=0 if the process is reversible)

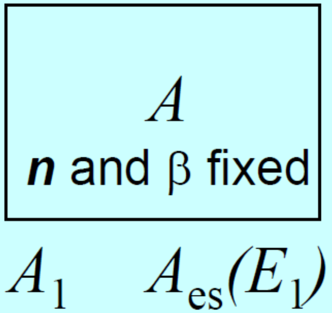
Review of basic concepts:

Maximum entropy principle,
State principle,
Fundamental relation for the SESs,
Temperature, pressure, and chemical potentials,
Gibbs relation

Review of basic concepts: Consequences of the (First&)Second Law:
Maximum Entropy Principle

Maximum entropy principle: among all the states with the same given values of the amounts of constituents, the parameters, and the energy, only the stable equilbrium state has the maximum value of the entropy.

(it is a direct consequence of the definition of s.e.s. and the statement of the Second Law; it holds in general for all systems)



Given the s.e.s. $A_{es}(E_1)$ with energy E_1 and any **other** state A_1 with the same E_1, we have:

$$S_1 < S_{es}(E_1)$$

Review of basic concepts: Consequences of the (First&)Second Law: Minimum Energy Principle (except for special systems)

Maximum entropy principle: among all the states with the same given values of the amounts of constituents, the parameters, and the energy, only the stable equilibrium state has the maximum value of the entropy.

(it is a direct consequence of the definition of s.e.s. and the statement of the Second Law; it holds in general for all systems)

A

n and β fixed

A_1 $A_{\mathrm{es}}(E_1)$

Given the s.e.s. $A_{\mathrm{es}}(E_1)$ with energy E_1 and any **other** state A_1 with the same E_1, we have:

$$S_1 < S_{\mathrm{es}}(E_1)$$

Minimum energy principle: among all the states with the same given values of the amounts of constituents, the parameters, and the entropy, only the stable equilibrium state has the minimum value of the energy.

(it holds in general for all systems with translational, rotational, and vibrational degrees of freedom, which from any state can receive energy in a w.p.)

(there are 'special' systems -- those that have an upper bound to the energy -- that admit two s.e.s. for every value of the entropy, one with minimum energy and positive temperature and the other with maximum energy and negative temperature)

Review of basic concepts: Consequences of the (First&)Second Law: (Stable equilibrium) State Principle and Fundamental Relation

State principle: among all the states with the same given values of the amounts of constituents, the parameters, and the energy, one and only one is a stable equilibrium state (Second Law) and therefore the value of any property is uniquely determined by the values of the amounts of constituents, the parameters, and the energy (*r*+*s*+1).

$$P = P(E, n_1, \ldots, n_r, \beta_1, \ldots, \beta_s)$$

Fondamental relation for the s.e.s. (in entropy form): it is the state principle applied to property entropy

$$S = S(E, n_1, \ldots, n_r, \beta_1, \ldots, \beta_s)$$

Fondamental relation for the s.e.s. in energy form: obtained by solving the above relation to obtain

$$E = E(S, n_1, \ldots, n_r, \beta_1, \ldots, \beta_s)$$

Taylor series expansion around a s.e.s. :

$$S(E + \Delta E, n, \beta) = S(E, n, \beta) + \left.\frac{\partial S}{\partial E}\right|_E \Delta E + \frac{1}{2}\left.\frac{\partial^2 S}{\partial E^2}\right|_E (\Delta E)^2 + \cdots$$

Review of basic concepts: Consequences of the (First&)Second Law:

Partial derivatives of the fundamental relation

Each partial derivative of the fundamental relation, either in entropy or energy form, represents a property of the family of s.e.s. of the system.

Note = we often consider systems that have volume as the only parameter, therefore, $S=S(E,\mathbf{n},V)$ and $E=E(S,\mathbf{n},V)$.

The (*absolute*) *temperature* is defined by

$$T=\left(\frac{\partial E}{\partial S}\right)_{\mathbf{n},V} \quad \text{or} \quad \left(\frac{\partial S}{\partial E}\right)_{\mathbf{n},V}=\frac{1}{T}$$

The *chemical potential of the i-th constituent* is defined by

$$\mu_i=\left(\frac{\partial E}{\partial n_i}\right)_{S,\mathbf{n},V} \quad \text{or} \quad \left(\frac{\partial S}{\partial n_i}\right)_{E,\mathbf{n},V}=-\frac{\mu_i}{T}$$

The *pressure* is defined by

$$p=-\left(\frac{\partial E}{\partial V}\right)_{S,\mathbf{n}} \quad \text{or} \quad \left(\frac{\partial S}{\partial V}\right)_{E,\mathbf{n}}=\frac{p}{T}$$

Notation for partial derivatives

Given the relation $z=z(x,y)$ the symbol

$$\left(\frac{\partial z}{\partial x}\right)_y=\frac{\partial z(x,y)}{\partial x}$$

Contains also the information about what are the other variables of the function being differentiated

Image Credits

Slide 2 and **Slide 18:**

Slide 16:

- Portrait of George N. Hatsopoulos courtesy of Jim Harrison (MIT News).
- Portrait of Joseph H. Keenan courtesy of the MIT Museum.

2.43 Advanced Thermodynamics
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