2.43 ADVANCED THERMODYNAMICS

Spring Term 2024
LECTURE 03

Room 3-442
Tuesday, February 13, 2:30pm - 4:30pm

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Room 3-351d

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.

only effect external to A
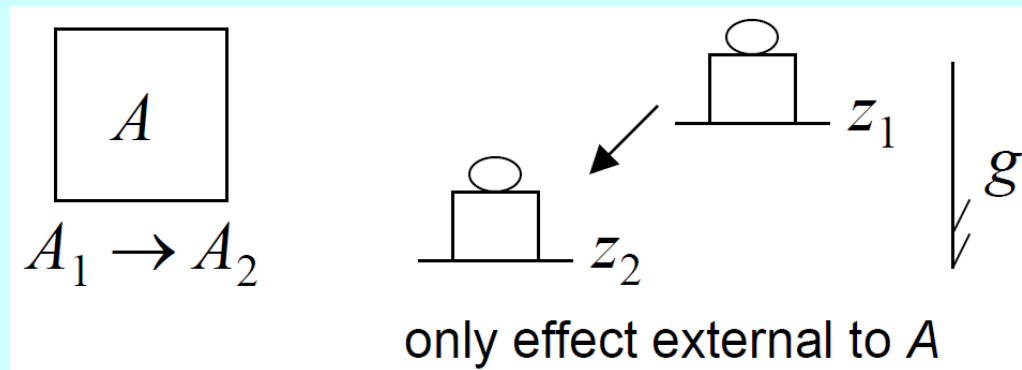
The most important consequence of the First Law is that it provides support to the **definition of property energy** for every (well-defined) system A in any state A_1
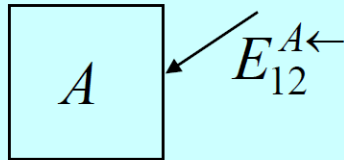
$$E_1^A = E_0^A - mg(z_1 - z_0)$$

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

Energy balance equation

Energy balance equation for a process for system A:
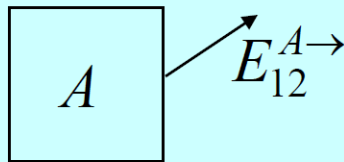
$$E_2^A - E_1^A = E_{12}^{A\leftarrow}$$

$A_1 \rightarrow A_2$

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

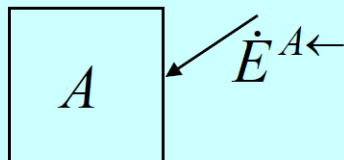$$E_2^A - E_1^A = -E_{12}^{A\rightarrow}$$

$A_1 \rightarrow A_2$

- $E_{12}^{A\rightarrow}$ 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)
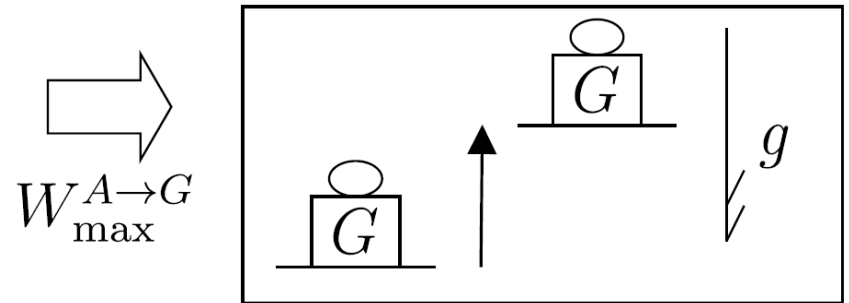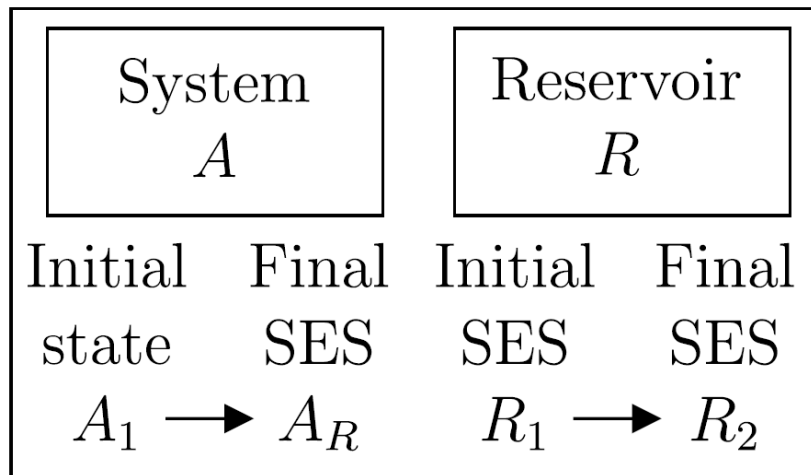
Second Law:

Assertion 1: in the subset of states of a system compatible with given values of the amounts of constituents n and of the parameters β, 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

System A		Reservoir R	
Initial state	Final SES	Initial SES	Final SES
$A_1 \longrightarrow A_R$		$R_1 \longrightarrow R_2$	

$W_{\max}^{A \to G}$

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

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

**Measurement procedure defining
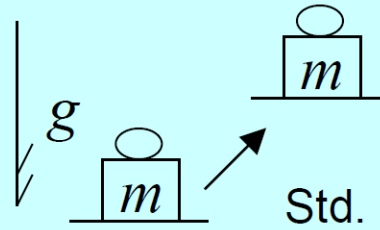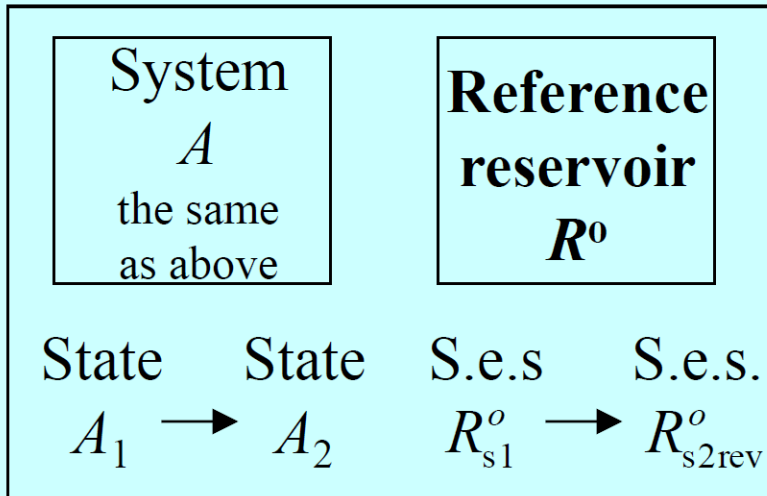the "constant temperature of a thermal reservoir"**

System A auxiliary to <u>this measure</u>	**Reservoir R** the object of <u>this measure</u>

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

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

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

System A the same <u>as above</u>	**Reference reservoir R^0**

State	State	S.e.s	S.e.s.
A_1	A_2	R^o_{s1}	R^o_{s2rev}
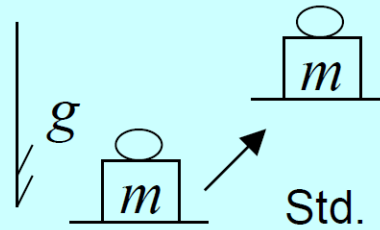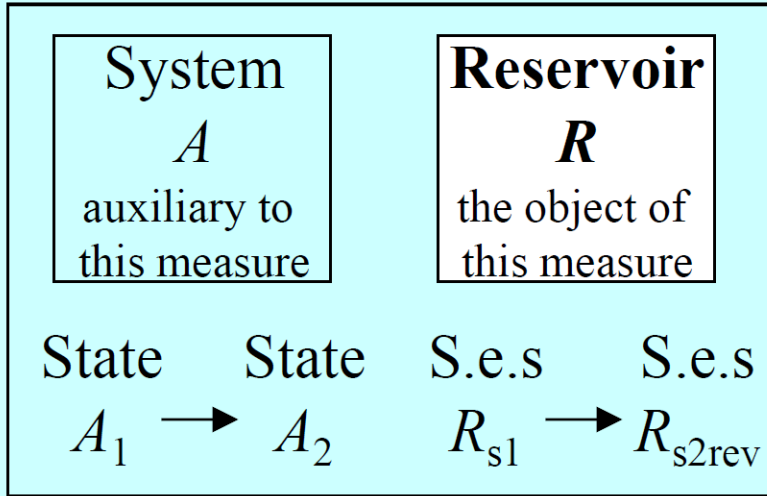
Std. rev. w.p. for AR^o
Measure the change in E^R

$$\frac{\left(E^R_{s2\,rev} - E^R_{s1}\right)_{A_1R_{s1} \underset{\text{w,rev}}{\Rightarrow} A_2R_{s2rev}}}{\left(E^{R^o}_{s2\,rev} - E^{R^o}_{s1}\right)_{A_1R^o_{s1} \underset{\text{w,rev}}{\Rightarrow} A_2R^o_{s2rev}}}$$

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

System A the object of this measure	**Reservoir R** auxiliary to this measure

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

State	State	S.e.s	S.e.s
A_1	$\rightarrow \quad A_0$	R_{s1}	$\rightarrow R_{s0rev}$
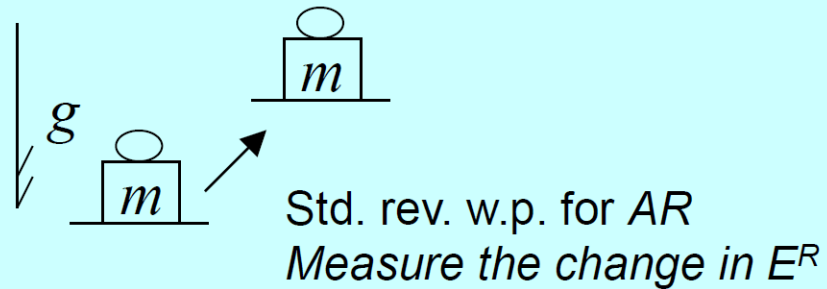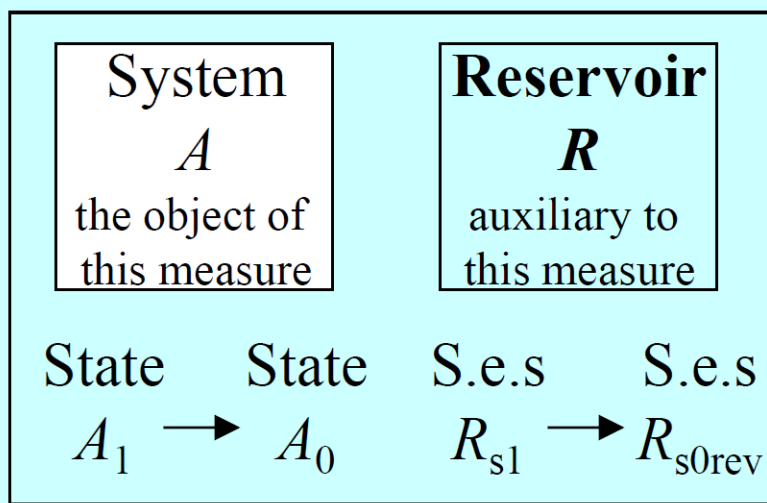
state A_0 is an arbitrarily chosen state to which we assign the arbitrary reference value S_0

The ratio:
$$\frac{\left(E^R_{s0rev} - E^R_{s1}\right)_{\substack{A_1 R_{s1} \Rightarrow A_0 R_{s0rev} \\ \text{w.rev}}}}{T_R}$$

• 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:
$$S_1 = S_0 + \frac{\left(E^R_{s0rev} - E^R_{s1}\right)_{\substack{A_1 R_{s1} \Rightarrow A_0 R_{s0rev} \\ \text{w.rev}}}}{T_R}$$

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

From the relation

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

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

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

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

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:
Theorems on criteria for the reversibility of a weight process
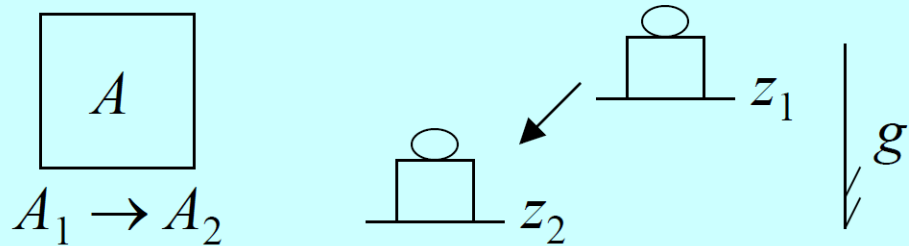
Theorem. The following equivalent conditions are necessary and sufficient for a <u>weight process</u> for system A to be reversible or irreversible:

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

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

$$S_2^A - S_1^A = S_{12}^{A\leftarrow} + \left(S_{irr}\right)_{12}^A$$
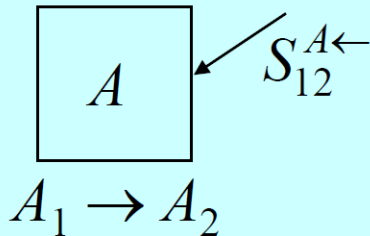
- $S_{12}^{A\leftarrow}$ entropy exchanged between *A* and its environment during the time interval from t_1 to t_2 (if positive, the net transfer is into *A*)

- $\left(S_{irr}\right)_{12}^A \geq 0$ 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 $t_2=t+dt)$

$$\frac{dS^A}{dt} = \dot{S}^{A\leftarrow} + \left(\dot{S}_{irr}\right)^A$$
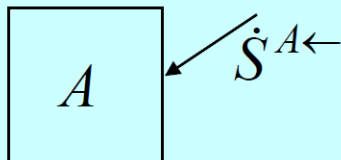
- $\dot{S}^{A\leftarrow}$ net rate of entropy transfer (into *A* if positive, out of *A* if negative)

- $\left(\dot{S}_{irr}\right)^A \geq 0$ rate of entropy generation by irreversibility within the system (=0 if the process is reversible)

Maximum Entropy Principle

and 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 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)

A

n and β fixed

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

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:

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

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 equilbrium 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)

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 equilbrium 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:

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

Partial derivatives of the fundamental relation
Gibbs relation

Fundamental relation for a system with volume as the only parameter

$$S = S(E, V, n_1, \dots, n_r)$$

Gibbs relation in entropy form

$$dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu_1}{T} dn_1 - \cdots - \frac{\mu_r}{T} dn_r$$

Fundamental relation in energy form

$$E = E(S, V, n_1, \dots, n_r)$$

Gibbs relation

$$dE = TdS - pdV + \mu_1 dn_1 + \cdots + \mu_r dn_r$$

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, $S=S(E, \textbf{n}, V)$ and $E=E(S, \textbf{n}, V)$.

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

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

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

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

The *pressure* is defined by

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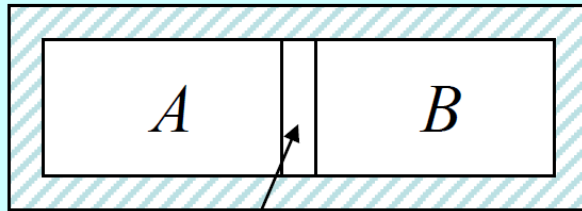

Notation for partial derivatives

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

Necessary conditions for mutual equilibrium

Two systems are in *mutual equilibrium* if the respective states are such that the composite system is in a stable equilbrium state.
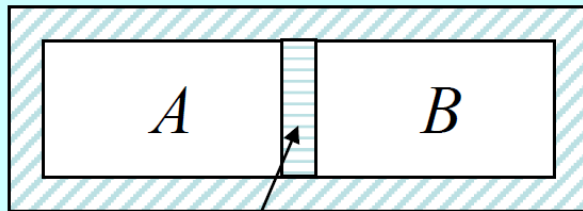

Diathermal wall

- *Equality of the **temperatures** of the two systems is a n.c. for m.e. if the two systems can exchange **energy**.*
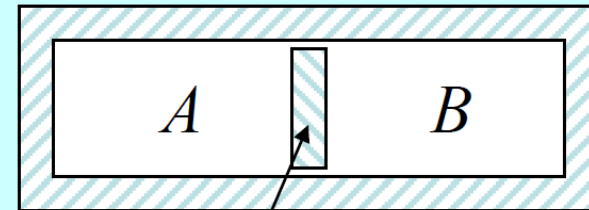
- *Equality of the **pressures** of the two systems is a n.c. for m.e. if the two systems can exchange **volume**.*

Movable pistone

Wall permeable
to the i-th costituent

- *Equality of the **chemical potentials of the i-th constituent** in the two systems is a n.c. for m.e. if the two systems can exchange **the i-th constituent**.*
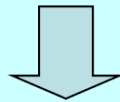
Graphical representation of basic concepts on

Energy vs Entropy diagrams
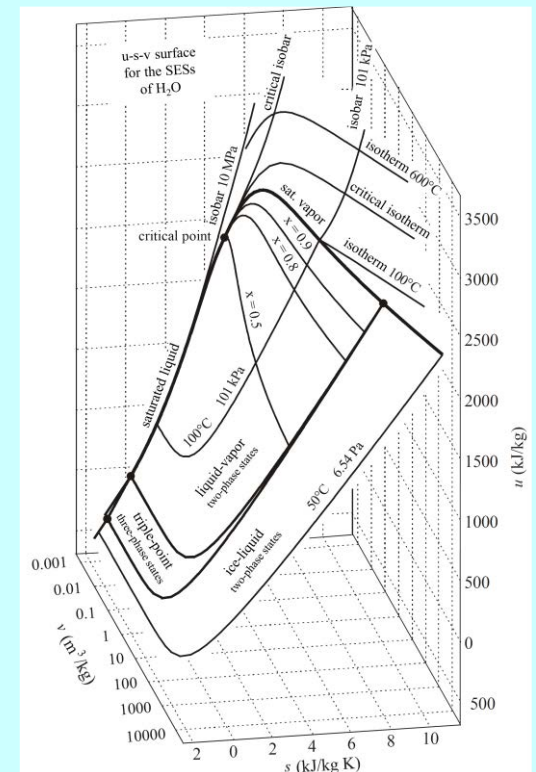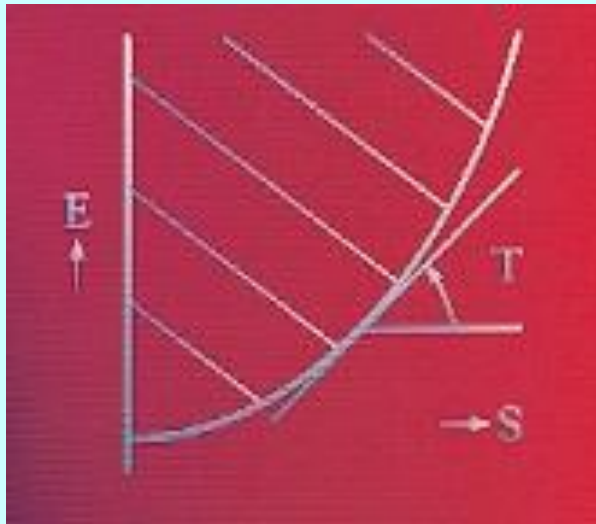
Graphical representation of basic concepts on **Energy vs Entropy diagrams:**
Projection of the state space on the E-S plane

- States are points in a multidimensional space with one axis for every amount, parameter, and independent property (almost always infinite dimensional)

- Consider the subspace corresponding to fixed values of the amounts of constituents and the parameters

- Project all points in this subspace on the two-dimensional energy vs entropy plane

⬇

We obtain a 2D representation of <u>all the states</u> of a system with given values of amounts and parameters

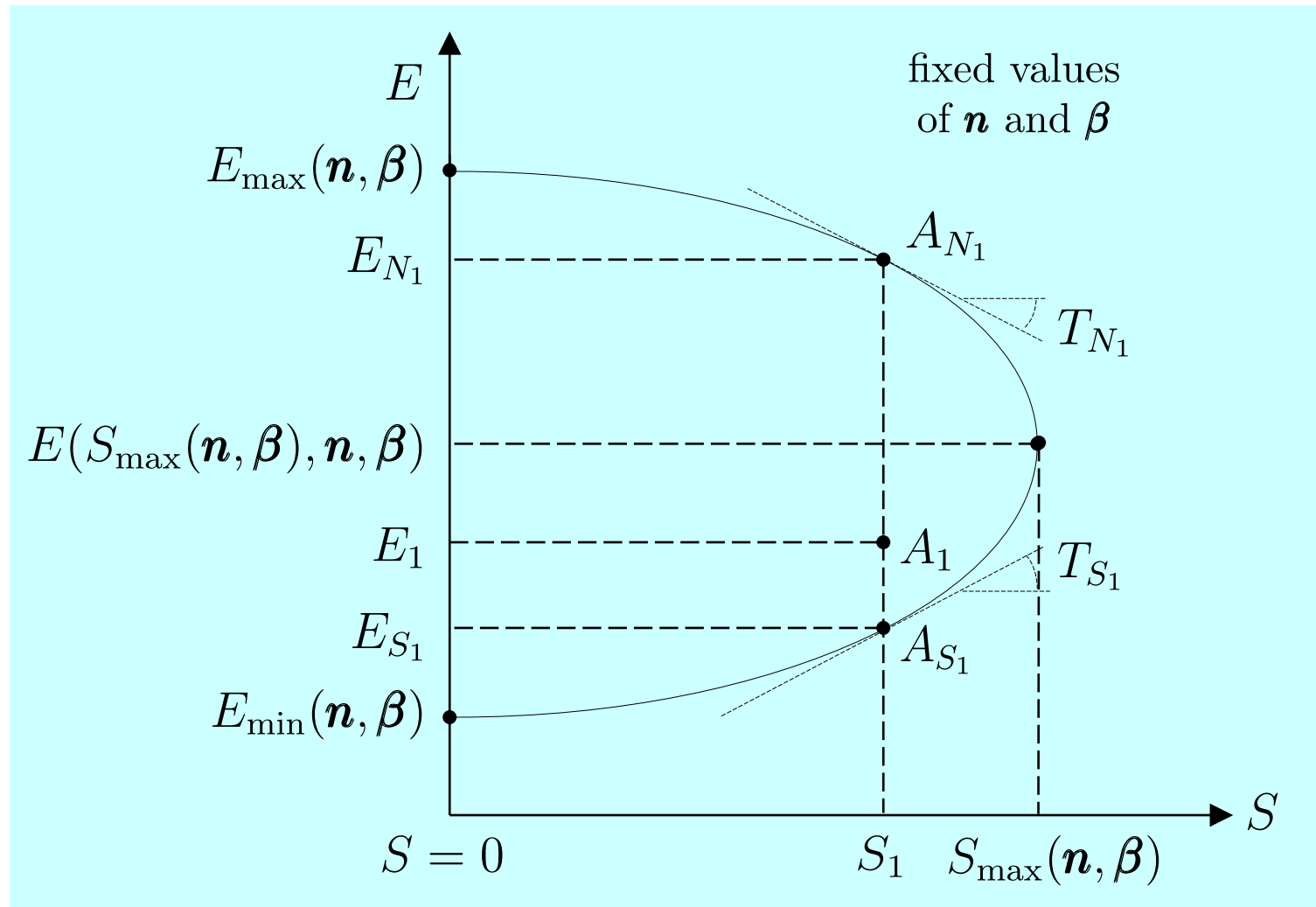# Graphical representation of basic concepts on **Energy vs Entropy diagrams:**
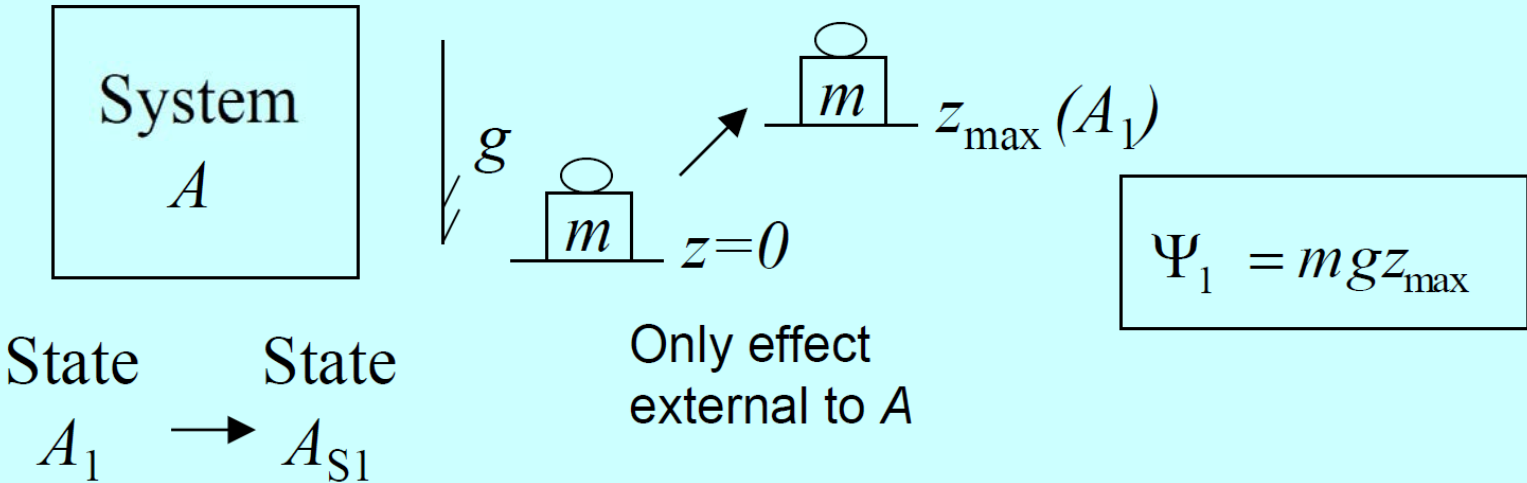## Representation of notSE states and SE states
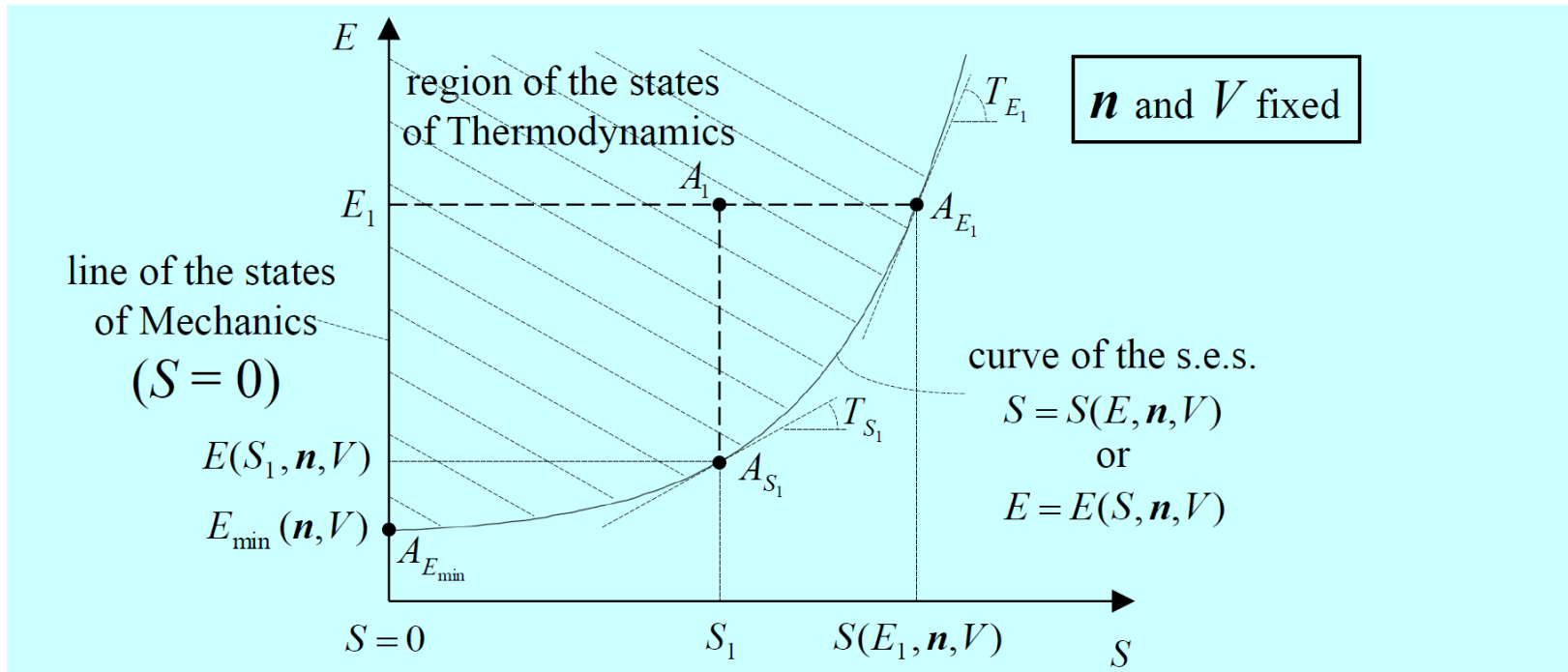
- A point in the region above the s.e.s. curve represents the projection of an infinite number of states that are not s.e.
- A point on the s.e.s. curve represents one and only one state, the unique s.e.s. with that value of the energy
- The slope of the tangent line to the s.e.s. curve is equal to the temperature of the s.e.s. represented by the point of contact
- Second Law and State Principle: for every value of E (horizontal line) there is a s.e.s. and it is the one with the maximum entropy
- The states considered by Mechanics are a subset of those considered by Thermodynamics, namely, those with zero entropy

Special systems with upper bounded energy

definition of property Adiabatic Availability

System

A

g m $z=0$ m z_{max} (A_1)

$$\Psi_1 = mgz_{max}$$

State A_1 → 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.
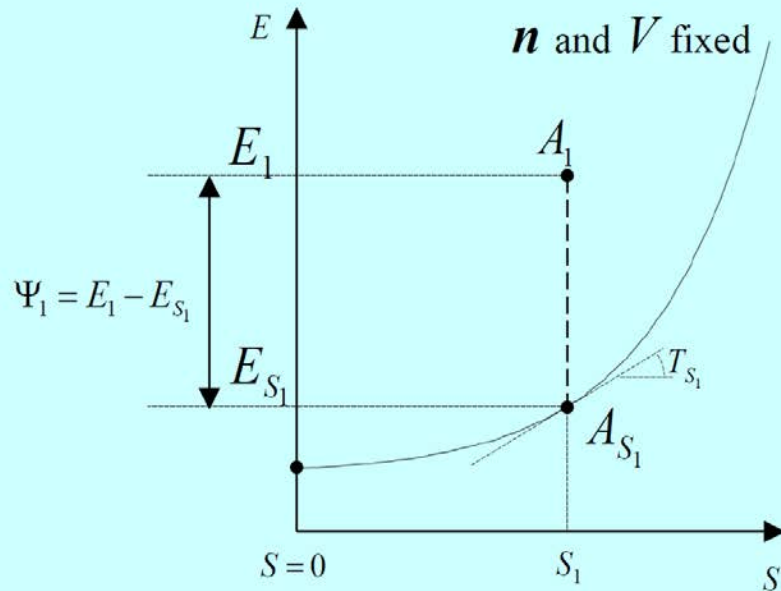
From the energy balance we obtain $$\Psi_1 = E_1 - E_{S1}$$

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.

$$\Psi_1 = E_1 - E_{S_1}$$

Adiabatic availability (Ψ): it is the part of the energy of A in a given state A_1 which can be transferred to a weight with no other external effects. It is obtained by means of rev.w.p. which ends in a stable equilibrium state, A_{s1}
- It is zero iff the state is a stable equilibrium state

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.
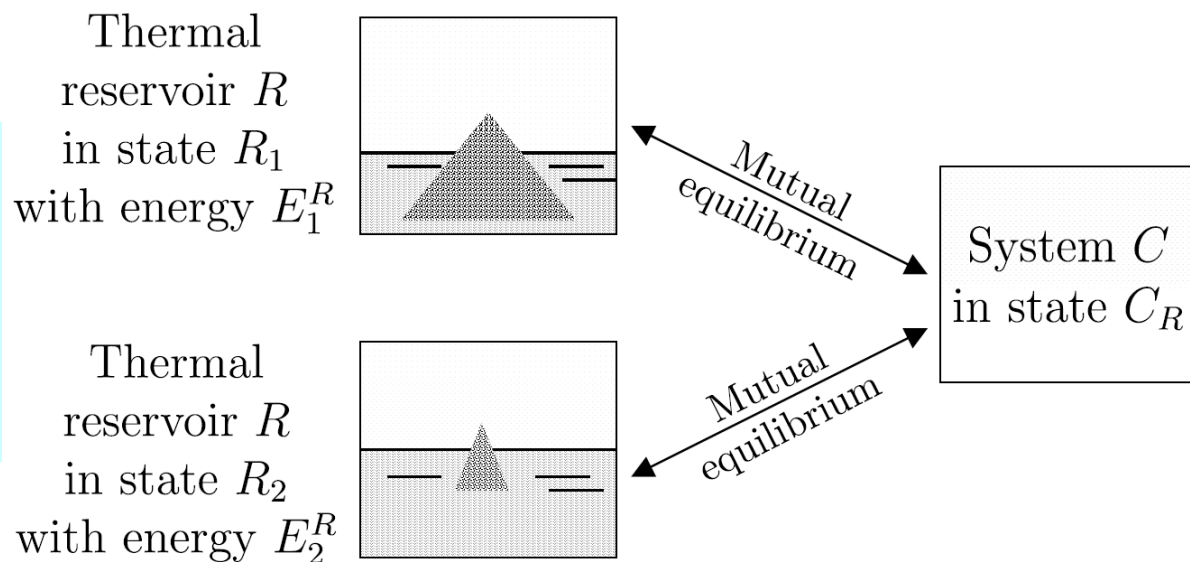
Thermal Reservoir (with constant amounts and parameters): a system R that in any of its stable equilibrium states is in mutual equilibrium with a given system C in a given state C_R
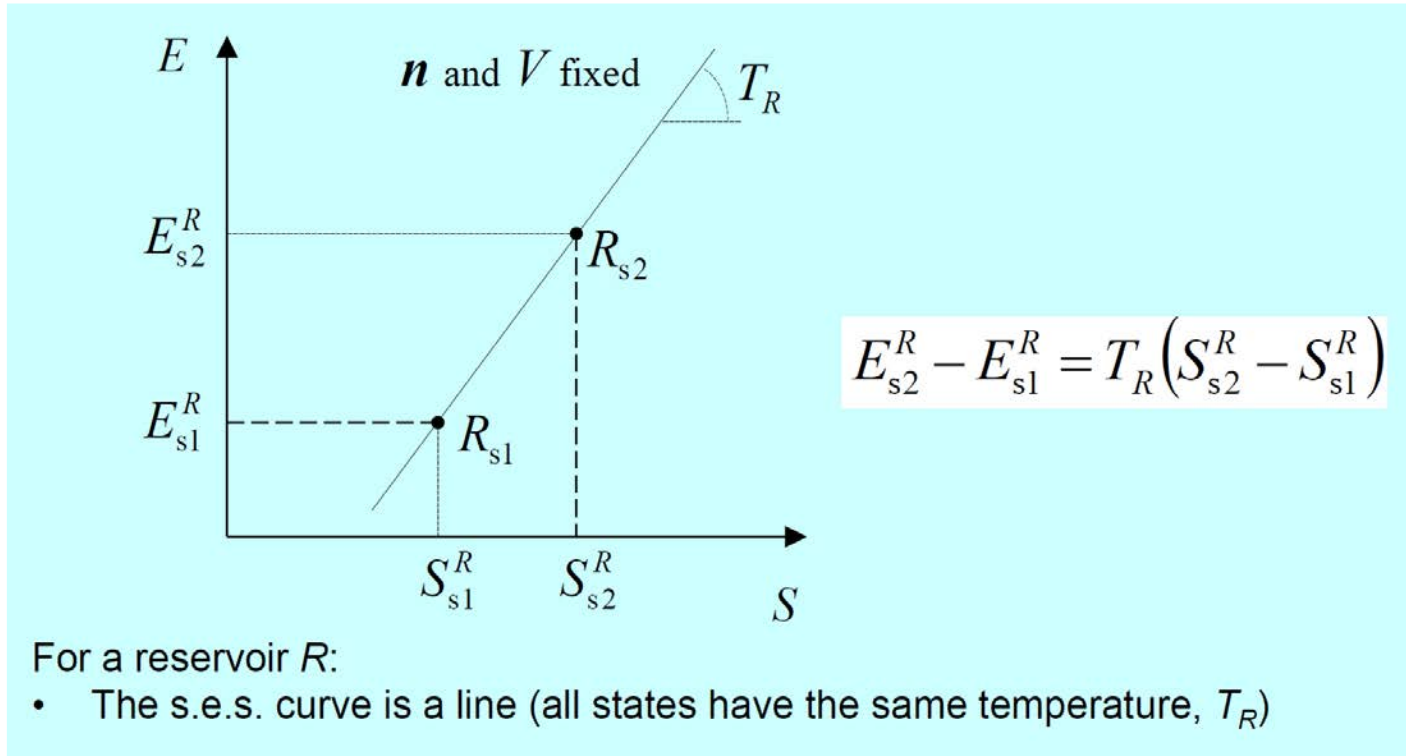
Example of a reservoir:
* H_2O *at the triple point*
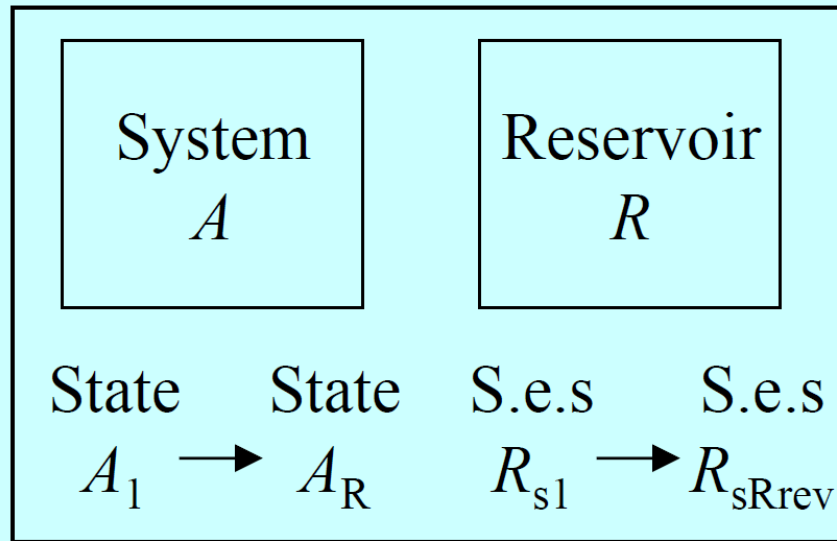
$$T_{pt} = 273.16 \, \text{K} \quad p_{pt} = 611.66 \, \text{Pa}$$

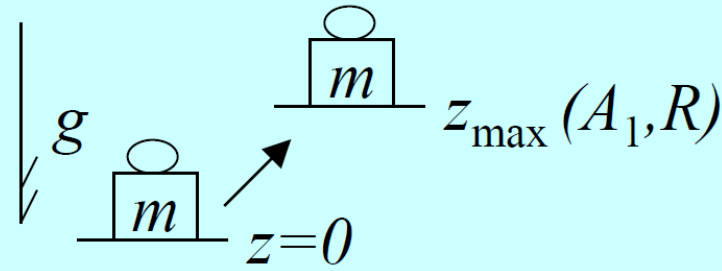as long as all the three phases are present in a finite amount

Thermal reservoir R in state R_1 with energy E_1^R

Thermal reservoir R in state R_2 with energy E_2^R

Mutual equilibrium

Mutual equilibrium

System C in state C_R

E

n and V fixed $\qquad T_R$

E_{s2}^R $\qquad R_{s2}$

$$E_{s2}^R - E_{s1}^R = T_R\left(S_{s2}^R - S_{s1}^R\right)$$

E_{s1}^R $\qquad R_{s1}$

S_{s1}^R $\qquad S_{s2}^R$ $\qquad S$

For a reservoir R:
*   The s.e.s. curve is a line (all states have the same temperature, T_R)

System A	Reservoir R
State $\quad$ State	S.e.s $\quad$ S.e.s
$A_1 \longrightarrow A_R$	$R_{s1} \longrightarrow R_{sRrev}$

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

g $\quad$ m $\quad$ $z_{\max}(A_1, R)$

m $\quad$ $z=0$

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.
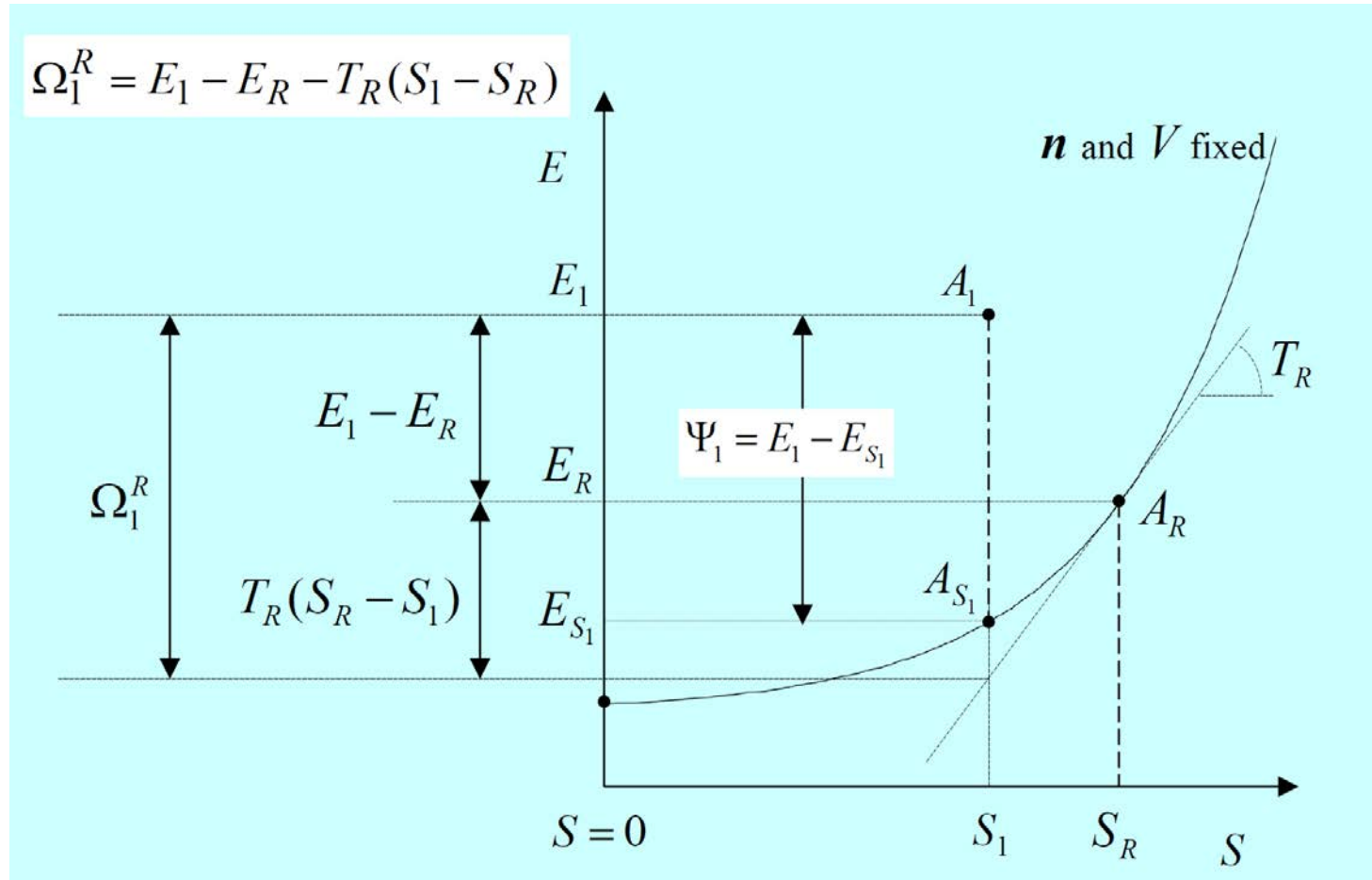
We denote the energy transferred to the weight by $\qquad$ from the energy balance

$$\Omega_1^R = mgz_{\max} = (E_1 - E_R) + (E_{s1}^R - E_{sRrev}^R)$$

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,

$$S_1 = S_R + \frac{E_{sRrev}^R - E_{s1}^R}{T_R} \qquad \longrightarrow \qquad \Omega_1^R = (E_1 - E_R) - T_R(S_1 - S_R)$$
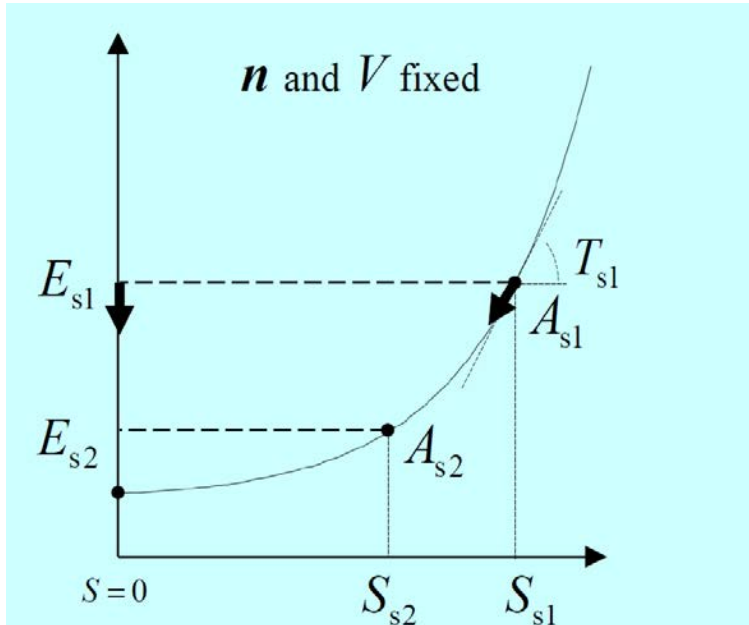
Graphical representation of basic concepts on **Energy vs Entropy diagrams:**

a system in a SES cannot
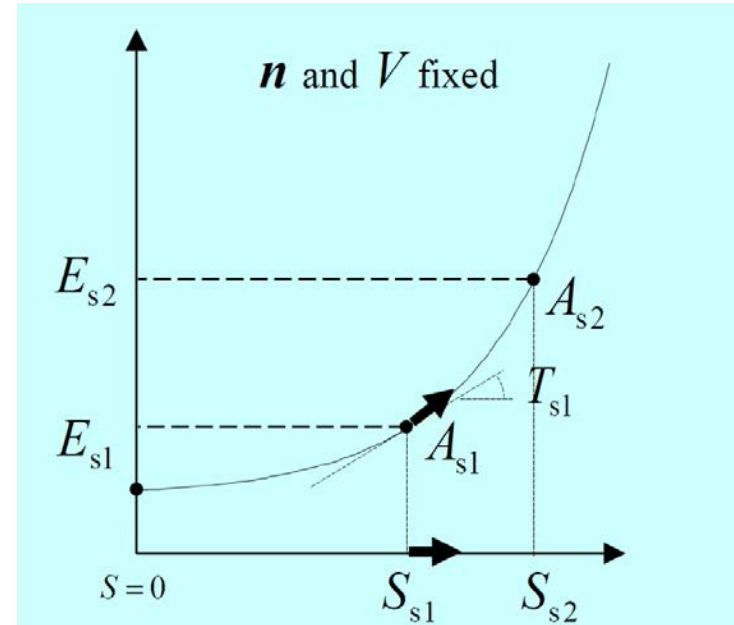## release energy unless...   receive entropy unless...

To <u>extract energy</u> from a system in a s.e.s., we must also extract entropy

$$S_{s1} - S_{s2} > (E_{s1} - E_{s2})/T_{s1}$$

To <u>give entropy</u> to a system in a s.e.s., we must also give energy

$$E_{s2} - E_{s1} > T_{s1}(S_{s2} - S_{s1})$$

Next:

Necessary conditions for mutual equilibrium

Image Credits

Slide 16:

- Figure on the cover of the book *Thermodynamics: Foundations and Applications* © Dover Publications. All rights reserved. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/help/faq-fair-use.

- u-s-v diagram for H_2O © Cartolibreria Snoopy. All rights reserved. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/help/faq-fair-use.

2.43 Advanced Thermodynamics
Spring 2024