2.43 ADVANCED THERMODYNAMICS

Spring Term 2024
LECTURE 01

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

Instructor: Gian Paolo Beretta
beretta@mit.edu
Room 3-351d

In 2024 Thermodynamics turns 200 years old!

RÉFLEXIONS

SUR LA

PUISSANCE MOTRICE

DU FEU

ET

SUR LES MACHINES

PROPRES A DÉVELOPPER CETTE PUISSANCE.

PAR S. CARNOT,

ANCIEN ÉLÈVE DE L'ÉCOLE POLYTECHNIQUE.

A PARIS,

CHEZ BACHELIER, LIBRAIRE,

QUAI DES AUGUSTINS, N°. 55.

1824.

Nicolas Léonard Sadi Carnot

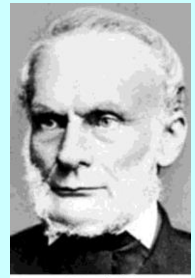
Here are only a few of the many great scientists who developed it

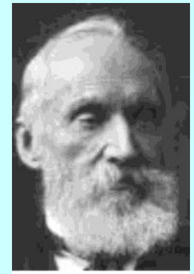

Sadi **Carnot** (1796-1832) French


James Prescott **Joule** (1818-1889) British

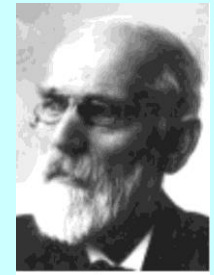

William J. M. **Rankine** (1820-1872) Scottish

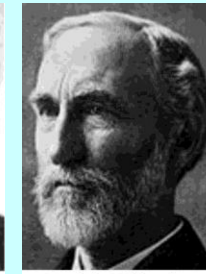

Hermann **von Helmholtz** (1821-1894) German


Rudolf **Clausius** (1822-1888) German


William Thomson **Lord Kelvin** (1824-1907) Scottish

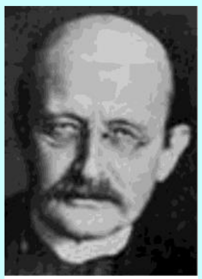

Francois J.D. **Massieu** (1832-1896) French

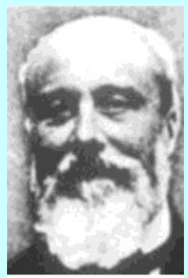

Johannes **van der Waals** (1837-1923) Dutch


Josiah Willard **Gibbs** (1839-1903) American


Ludwig **Boltzmann** (1844-1906) Austrian


Jacobus **van't Hoff** (1852-1911) Dutch

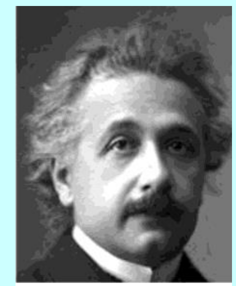

Max **Planck** (1858-1947) German


Pierre **Duhem** (1861-1916) French


Walther Hermann **Nernst** (1864-1941) German

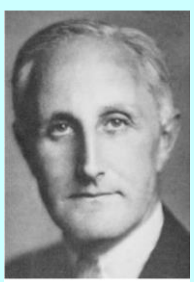

Arnold **Sommerfeld** (1868-1951) German


Constantin **Caratheodory** (1873-1950) Greek


Albert **Einstein** (1879-1955) German-Swiss-American

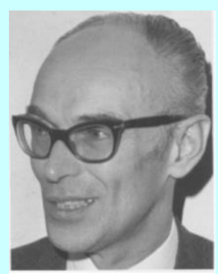

Joseph Henry **Keenan** (1900-1977) American


Enrico **Fermi** (1901-1954) Italian


Edward Armand **Guggenheim** (1901–1970) British

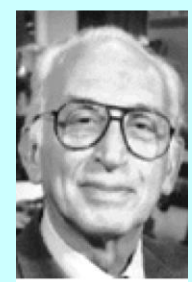

Lars **Onsager** (1903-1975) Norwegian


Hans **Ziegler** (1910-1985) Swiss


Sybren Ruurds **de Groot** (1916-1994) Danish


Ilya **Prigogine** (1917-2003) Belgian

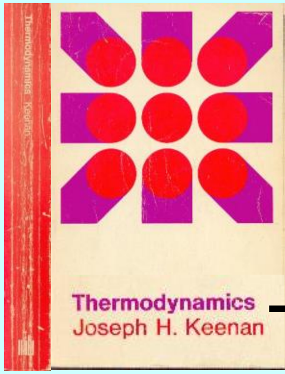

Peter **Mazur** (1922-2001) Dutch


George N. **Hatsopoulos** (1927-2018) Greek-American


John M. **Prausnitz** (1928-) German-American

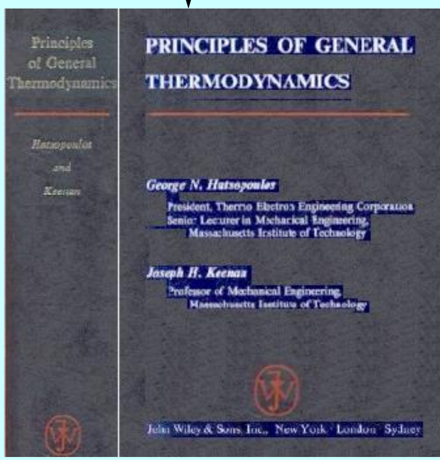
Reference books by MIT-MechE members of the “Keenan School”

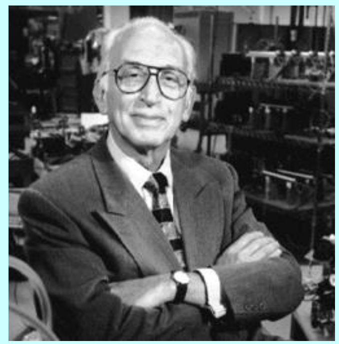
1941



The concept of availability

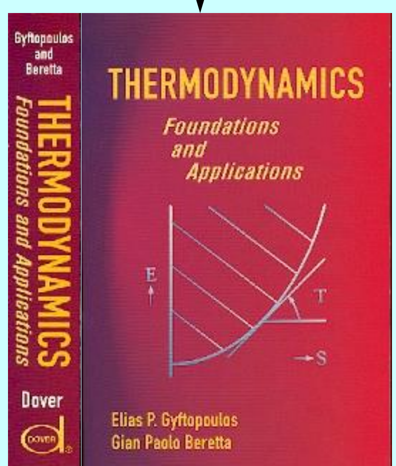
1965





The Hatsopoulos-Keenan unifying statement of the Second Law (based on the role of stability at thermodynamic equilibrium)

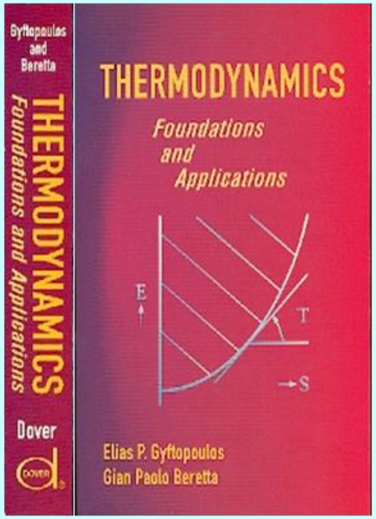
1991 (2005)



Rigorous axiomatic foundations
Definition of entropy valid for non-equilibrium states

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

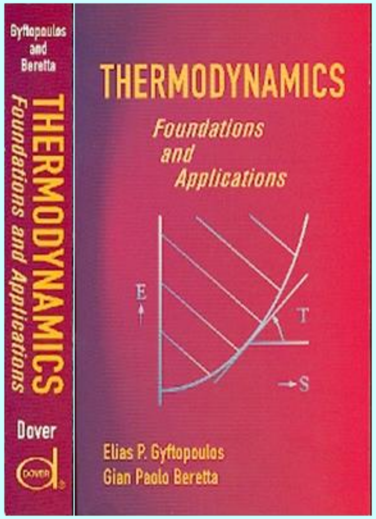
Contents:

- 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

Part II: chemical potentials and multicomponent equilibria

Contents:

- Modeling ideal and nonideal gas mixtures and solutions
- Mutual equilibrium across semi-permeable membranes
- Minimum work of separation, maximum work of mixing
- Osmotic pressure
- Liquid-vapor and liquid-liquid phase equilibria
- Metastable states and spinodal decomposition
- Modeling chemically reacting mixtures
- Chemical equilibrium
- Chemical kinetics standard model
- Electrochemical potentials



Part III: nonequilibrium states and irreversible processes in continua

Contents:

- Local and constrained equilibrium modeling of multicomponent flows
- Simultaneous diffusion of energy, mass, charge, and entropy modeled
- Extending the concept of heat interaction
- Onsager reciprocal relations valid near equilibrium
- Ziegler principle of maximal entropy production
- Curie symmetry principle
- Applications to:
  - Heat transfer in anisotropic materials (Righi-Leduc effect)
  - Thermodiffusive cross effects (Soret, Dufour, membrane thermo-osmosis)
  - Thermoelectric cross effects (Seebeck, Peltier)
  - Electrokinetic phenomena (electro-osmosis, streaming potential, electrophoresis, sedimentation potential)
- Recent research efforts attempting to extend thermodynamics to the realms of:
  - Far-nonequilibrium phenomena
  - Few-particle systems

Grading policy:

- Midterm take-home assignment on allocation: 15%
- Four midterm take-home quizzes on Parts I and II: 10% each
- Final oral exam focused on Part II and III: 45%

- Grading type: Letter grades (A-F) with ±
- Final grade: weighted average (rounded upwards)
  based on A=5, B=4, C=3, D=2, F=0, ±=±0.33

- Each take-home assignment and quiz requires you to create a brief (max 5 min) video, explaining a topic using instructor-provided viewgraphs.
- No need to memorize formulas.
- The emphasis is on probing your oral capacity to provide precise and effective explanations.
- The final oral exam follows a similar approach. Typically lasts no more than 30 minutes, and focuses on topics from the second and third parts of the course. Conducted in person during final exam week.

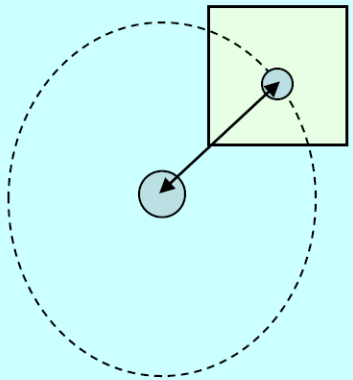
Review of basic concepts and definitions:

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

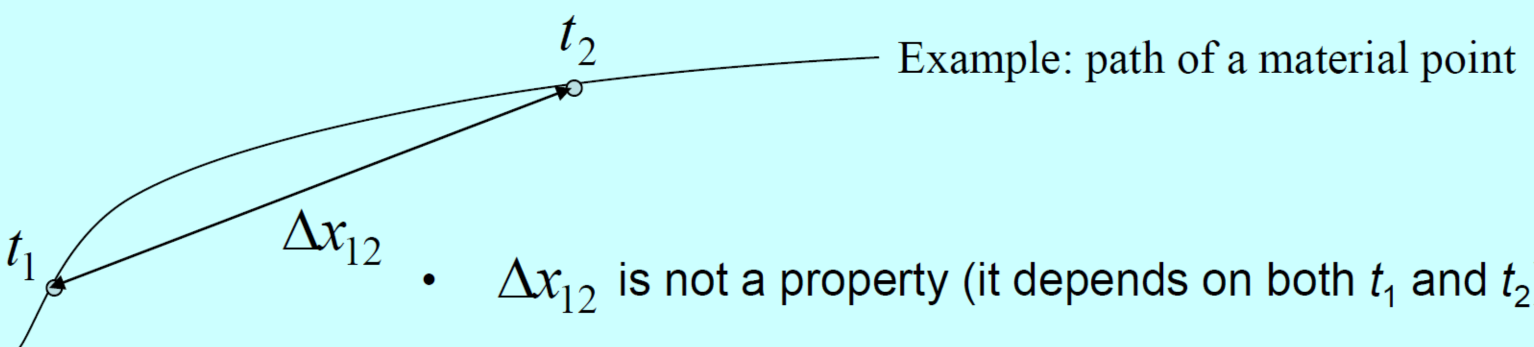
$\Rightarrow$ The electron by itself cannot qualify as a *system*

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

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



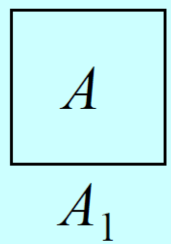
- Δx_{12} is not a property (it depends on both t_1 and t_2)
- $\dfrac{\Delta x_{12}}{t_2 - t_1}$ is not a property (it depends on both t_1 and t_2)
- $w_1 = \lim_{t_2 \to t_1} \dfrac{\Delta x_{12}}{t_2 - t_1}$ is a property (it depends on t_1 only)

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

Time evolution of the state of the system:

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**

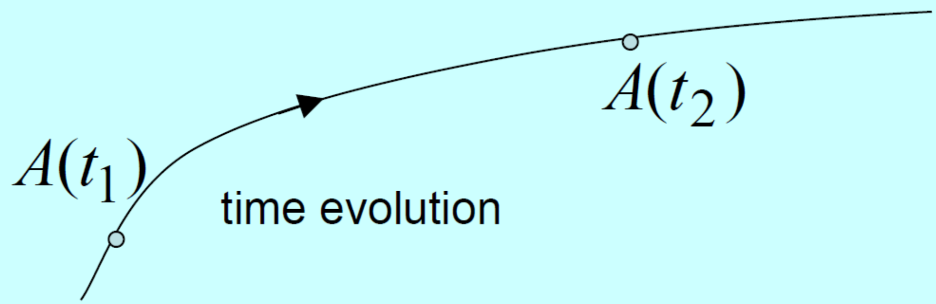
general LAWS of time evolution

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:

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



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:

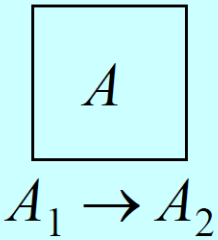
1. **First law** of T.
2. **Second law** of T.

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**

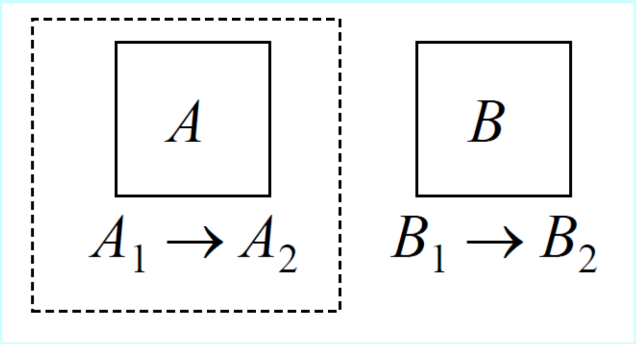
Process: it is specified by

- 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



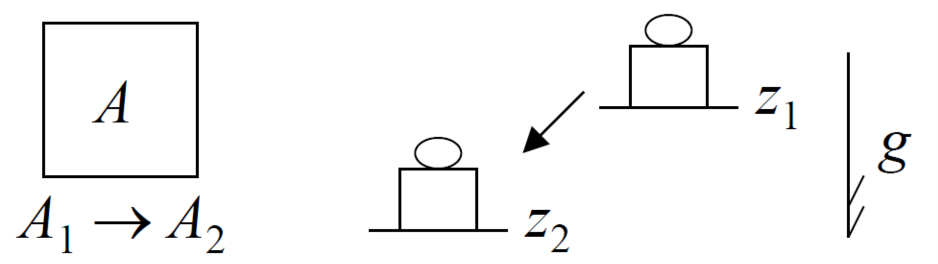
Review of basic concepts: **definition of**

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)



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:

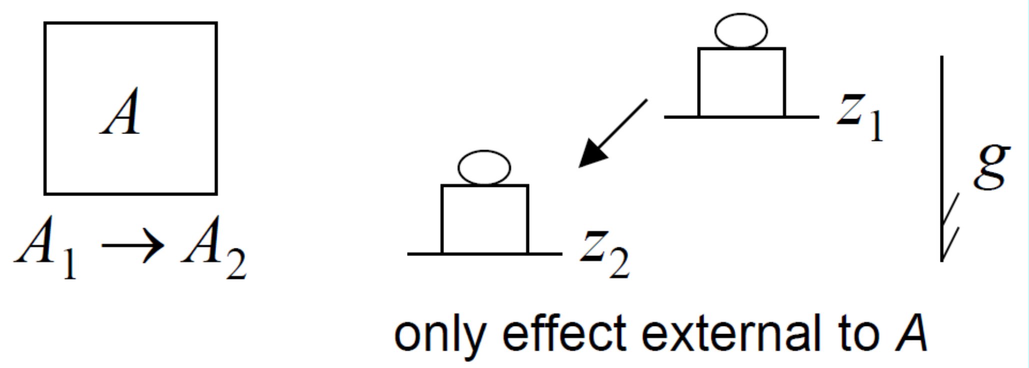
First Law,
definition of Energy,
Energy balance

Statement of the First Law of Thermodynamics

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.

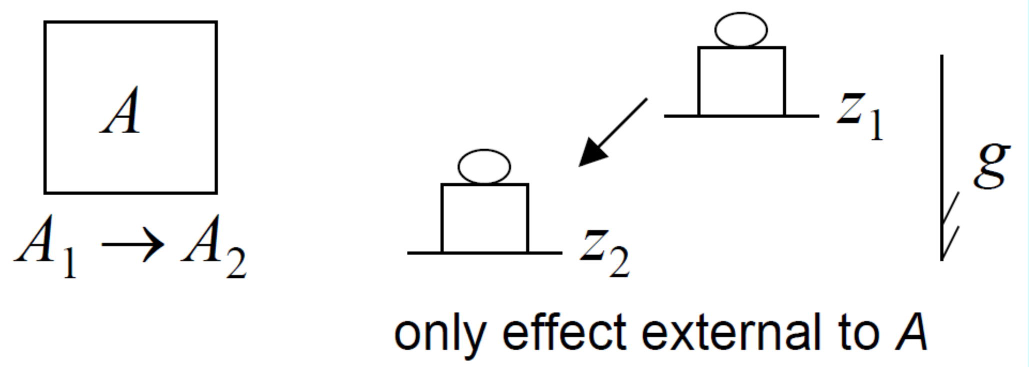


Review of basic concepts: Main consequence of the First Law: definition of property Energy

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.



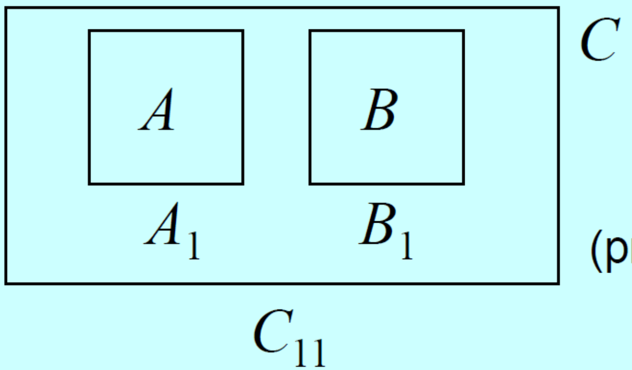
The most important consequence of the First Law is that it provides support to the **definition of property energy** for every (well-defined) system *A* in any state A_1

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

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

Consequences of the First Law: additivity and conservation of Energy

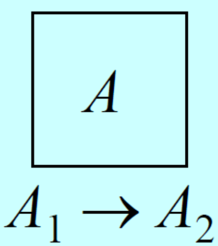
Additivity of energy: given two systems *A* and *B* and the composite system *C*=*AB*, for every state we have

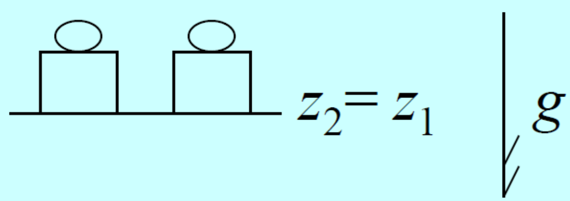


$$E_{11}^{C} = E_1^{A} + E_1^{B}$$

(provided we choose $E_{00}^{C} = E_0^{A} + E_0^{B}$)

Conservation of energy: in a process with no net external effects (such as a spontaneous process), the energy rimans costant

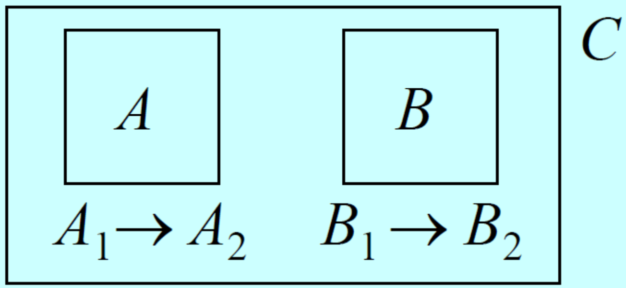




$$E_2^{A} = E_1^{A}$$

Review of basic concepts: Consequences of the First Law: exchangeability of Energy via interactions

Exchangeability of energy: consider a 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



$$C_{11} \rightarrow C_{22}$$

$$E^C_{22} = E^C_{11}$$

additivity ⇓

$$E^A_2 + E^B_2 = E^A_1 + E^B_1$$

⇓

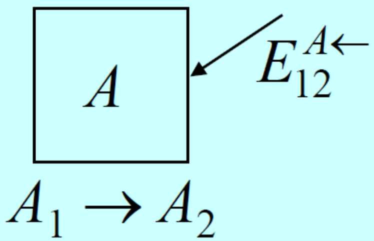
$$E^A_2 - E^A_1 = -(E^B_2 - E^B_1)$$

- If the energy of B has decreased, the energy of A has increased by an equal amount, therefore, we can say that energy has been transferred from B to A
- $E^{A\leftarrow B}_{12} = -(E^B_2 - E^B_1)$, if positive, denotes the energy that A received from B,
- otherwise, $-E^{A\leftarrow B}_{12} = E^{A\rightarrow B}_{12}$, if positive, denotes the energy that A gives to B

Notice: «If anything is conserved, it has to be conserved locally!».
This follows from the principle of relativity. For this and much more, view the wonderful Feynman lecture on «The Great conservation principles» (1964).

Energy balance equation

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

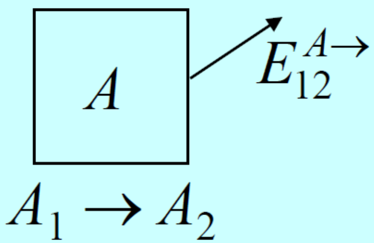


$$E_2^A - E_1^A = E_{12}^{A\leftarrow}$$

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

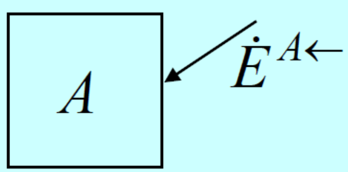
$E_{12}^{A\leftarrow}$



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

- $E_{12}^{A\rightarrow}$ 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:

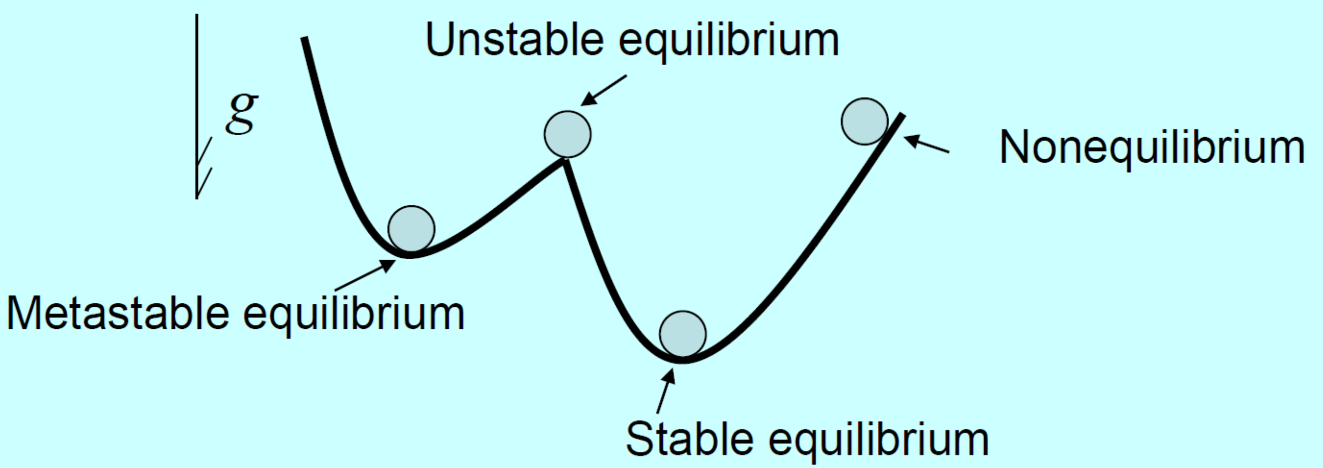
- *whether they change or not as a function of time*
- *whether such time behavior is due or not to interactions with other systems*

	…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?

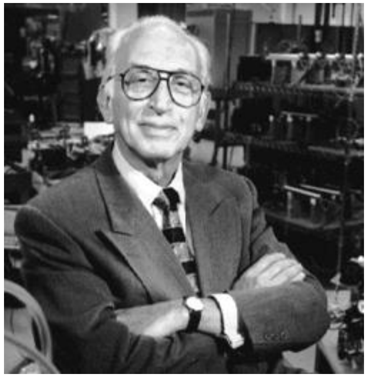
Answer in the domain of Mechanics:

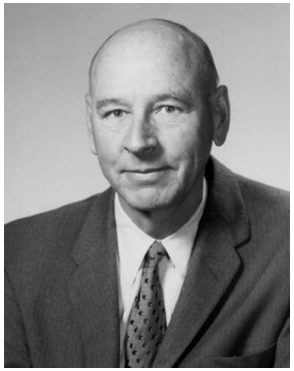
One and only one: the state with minimum energy, $E_g(n,\beta)$

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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Slide 5 and **Slide 6:**

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