

Important Points from Last Lecture

- Macroscopic systems in equilibrium are described by thermodynamic coordinates such as V , N_i , etc.
- All thermodynamic coordinates are either extensive or intensive.
- Thermodynamic coordinates can be either constrained or unconstrained depending on the experimental situation.
- A macroscopic system possesses well-defined internal energy, U . This energy is the sum of the kinetic energy of atoms and molecules in the system and the potential energy of mutual interactions between the atoms and molecules. U is an extensive thermodynamic coordinate.
- Energy is conserved

$$dU = \delta Q + \delta W$$

- W and Q are not thermodynamic coordinates, a state of a system cannot be characterized by W and Q . W and Q depend on history, on the process.

Postulates of Thermodynamics

- Thermodynamics is developed on the basis of **four postulates**.
- These postulates is just a concise way of summing up a large body of experimental facts about macroscopic systems.
- There are a **few different but equivalent ways of formulating the postulates** (they are sometimes called “the laws of thermodynamics”).
- For convenience, we will use the postulates as they are formulated in the Callen’s textbook.

Postulate I

Equilibrium states of a simple macroscopic system are completely described by the values of its internal energy and the values of all other extensive coordinates of the system.

For a liquid or gas: $(U, V, N_1 \dots N_m)$ – completely define the equilibrium state of the multi-component system.

For a crystalline solid: $(U, N_1 \dots N_m, \text{linear dimensions, twisting and bending angles, the amount of atomic ordering})$ – completely define the equilibrium state of the multi-component system.

Postulate I

There exist particular states (called equilibrium states) of simple systems that, macroscopically, are characterized completely by the internal energy U , the volume V , and the mole numbers $N_1, N_2, \dots, N_r$ of the chemical components.

For a liquid or gas: $(U, V, N_1 \dots N_m)$ – completely define the equilibrium state of the multi-component system.

For a crystalline solid: $(U, N_1 \dots N_m, \text{linear dimensions, twisting and bending angles, the amount of atomic ordering})$ – completely define the equilibrium state of the multi-component system.

The Basic Problem of Thermodynamics

Equilibrium states are completely defined by the full set of extensive coordinates of the system ($U, V, N_1 \dots N_m, \dots$).

Some of these extensive coordinates (parameters) may be fixed (constrained) by the environment.

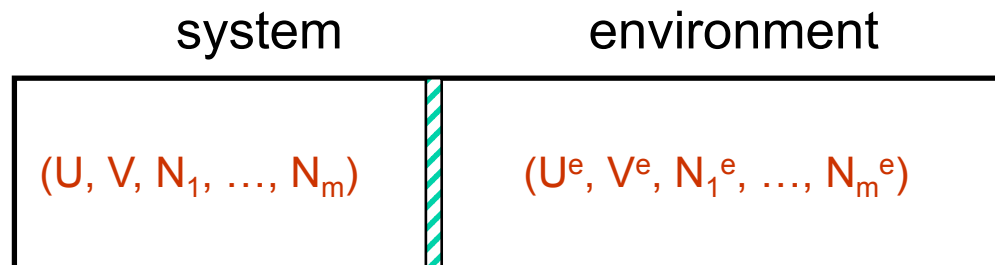
The main problem of thermodynamics:

Determine the equilibrium state that eventually results after the removal of internal constraints in a closed, composite system.

Example: How many mole numbers of air are there in an open 1-liter bottle at room temperature and atmospheric pressure?

Model of a Thermodynamic System and its Environment

- The **system** of interest + its **environment** form a large **super-system** (or **composite system**) which is isolated from the rest of the world.
- Isolated means that neither energy nor matter can flow in or out of the super-system
- The system of interest **is not isolated** from the **environment** when at least one of the **thermodynamic coordinates** of the system **is not constrained**



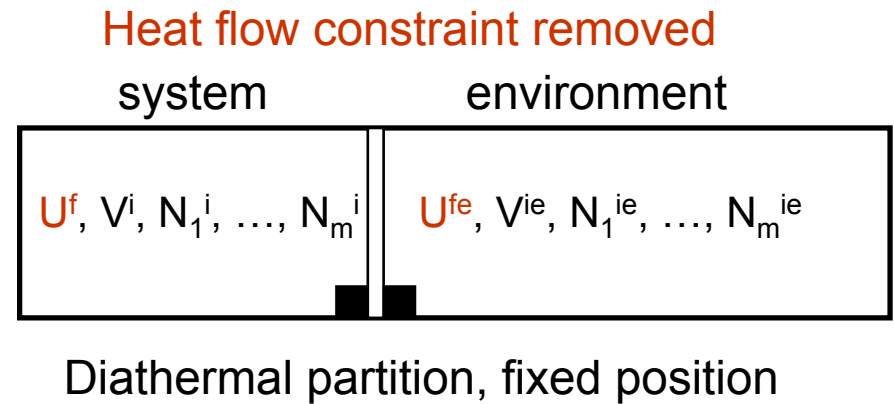
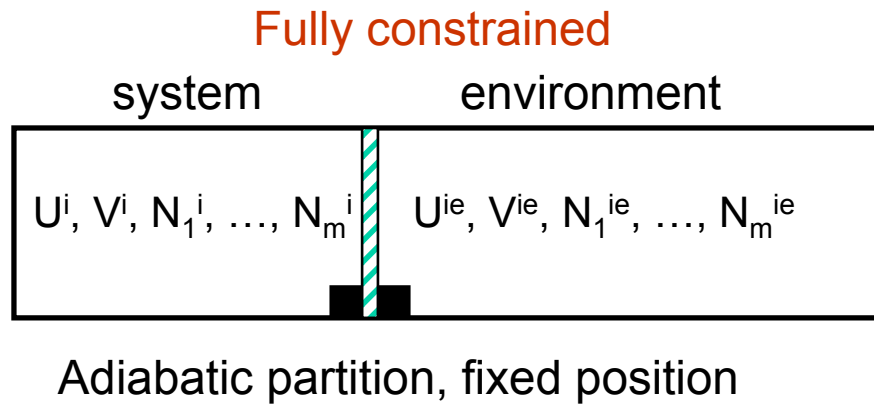
Barrier transparent to at least one of the thermodynamic coordinates ($U, V, N\dots$)

The Basic Problem of Thermodynamics: Role of the Environment

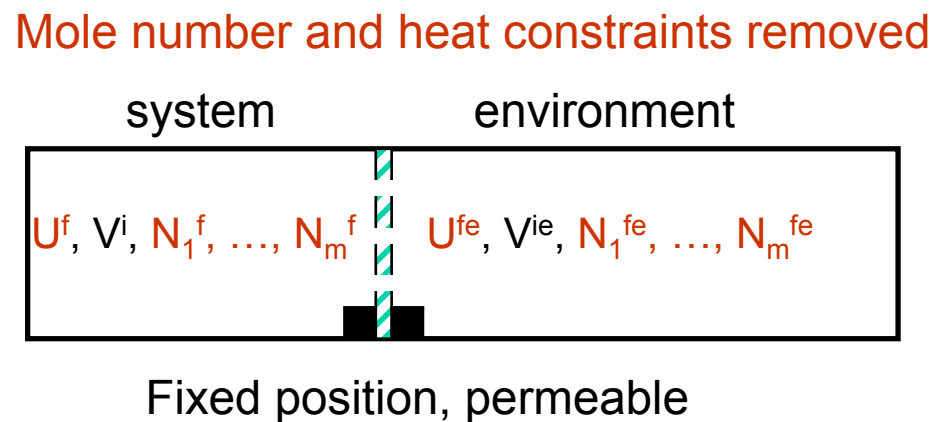
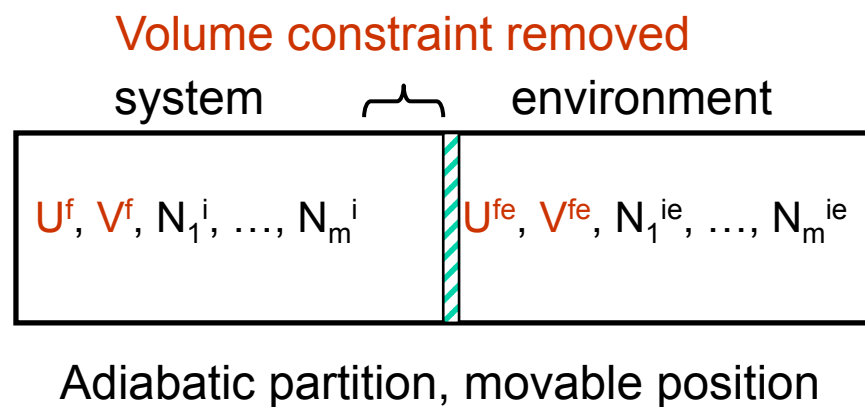
- The values of constrained coordinates of the system are fixed.
- The values of unconstrained coordinates depend on the state of the environment.
- Therefore, the state of the system with at least one unconstrained coordinate depends on the state of its environment!

Example: the volume of the bottle is fixed (1 liter). The mole number of air in the bottle is not fixed, so it may depend on the temperature of the environment.

System + Environment: Constraint Removed



System + Environment: Constraint Removed



Criterion for Equilibrium Values of Unconstrained Coordinates

Postulate II

There exists a function (called the entropy S) of the extensive parameters of any composite system, defined for all equilibrium states and having the following property: The values assumed by the extensive parameters in the absence of an internal constraint are those that **maximize the entropy** over the manifold of constrained equilibrium states.

$$S_{\text{equilibrium}}(U, V, N_1, \dots, N_m; U^e, V^e, N_1^e, \dots, N_m^e) =$$

$$\text{Max } \{S(U, V, N_1, \dots, N_m; U^e, V^e, N_1^e, \dots, N_m^e)\}_{\text{all unconstrained coordinates}}$$

- In statistical mechanics the entropy is the logarithm of the number of microstates that the system can attain (lost info).
- One can say that thermodynamics is a branch of physics that deals with energy and information.

Criterion for Equilibrium Values of Unconstrained Coordinates

Postulate II

There exists a function (called the entropy S) of the extensive parameters of a macroscopic system and its environment that is maximized by the equilibrium values of the unconstrained extensive coordinates.

$$S_{\text{equilibrium}}(U, V, N_1, \dots, N_m; U^e, V^e, N_1^e, \dots, N_m^e) =$$

$$\text{Max } \{S(U, V, N_1, \dots, N_m; U^e, V^e, N_1^e, \dots, N_m^e)\}_{\text{all unconstrained coordinates}}$$

- In statistical mechanics the entropy is the logarithm of the number of microstates that the system can attain (lost info).
- One can say that thermodynamics is a branch of physics that deals with energy and information.

The Fundamental Relation

The relation that gives the entropy as a function of the extensive coordinates is called the **fundamental relation**:

$$S = S(U, V, N_1, \dots, N_m; U^e, V^e, N_1^e, \dots, N_m^e)$$

The fundamental relation contains **all thermodynamic information** about a thermodynamic system.

Properties of Entropy – Postulate III

Postulate III

The **entropy** of a composite system is extensive (additive over the constituent subsystems). It is a continuous, differentiable and monotonically increasing function of the internal energy.

It follows from the Postulate III that the entropy of an isolated super-system is equal to the sum of the entropies of the system of interest and its environment:

$$S(U, V, N_1, \dots, N_m; U^e, V^e, N_1^e, \dots, N_m^e) = S(U, V, N_1, \dots, N_m) + S(U^e, V^e, N_1^e, \dots, N_m^e)$$

This postulate ensures that we can solve the fundamental relation for **U** and obtain a single-valued function for the internal energy as a function of extensive coordinates.

$$U(S, V, N_1, \dots, N_m; U^e, V^e, N_1^e, \dots, N_m^e)$$

Properties of Entropy – Postulate IV

Postulate IV

The entropy of any system vanishes ($S = 0$) in the state for which $(\partial U / \partial S)_{V, N_1 \dots N_m} = 0$.

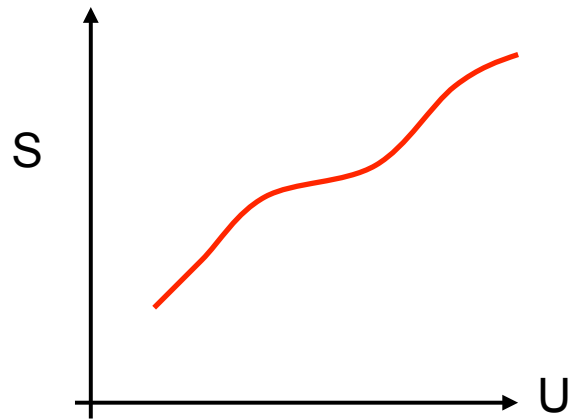
As we will see later, $(\partial U / \partial S)_{V, N_1 \dots N_m} = T$ (temperature). So $S = 0$ at $T = 0$.

Postulate IV is also known as “the Nernst postulate” or “the third law of thermodynamics”.

Postulate IV is much less general and important than postulates I, II and III. In fact, there are systems where $S \neq 0$ at $T=0$ because the system is not in equilibrium (e.g., some frustrated magnets, some glasses).

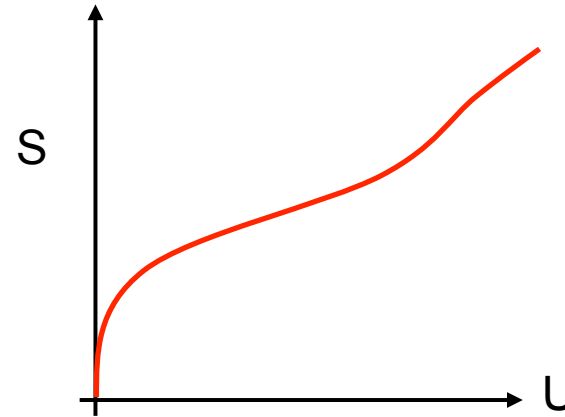
Possible Shapes of S versus U curves

Monotonically increasing



Postulate III

Tangential to the S -axis at $S = 0$

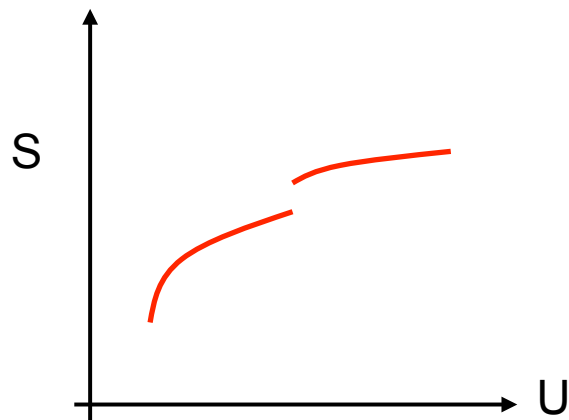


Postulate IV

$$(\partial U / \partial S)_{V, N_1 \dots N_m} = 0. \rightarrow (\partial S / \partial U)_{V, N_1 \dots N_m} = \infty$$

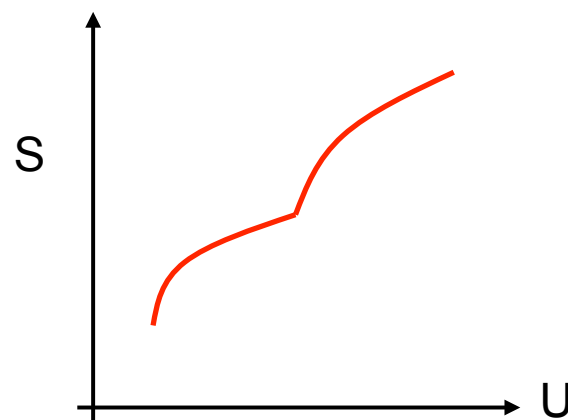
Forbidden Shapes of S versus U curves

Discontinuities are not possible
(continuity)



Postulate III

Kinks are not possible
(differentiability)



Postulate III

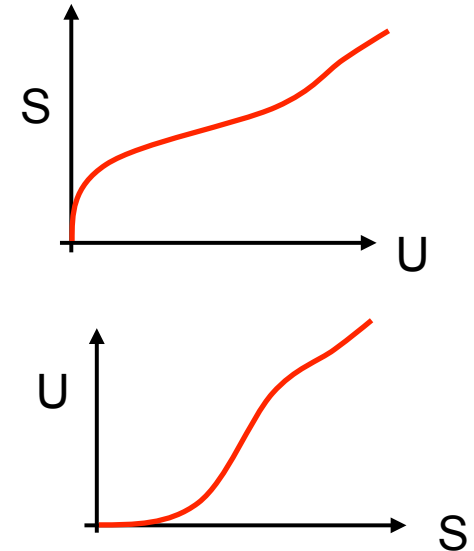
The Fundamental Relation

If the **fundamental relation** is known, everything is known about the system:

$$S = S(U, V, N_1, \dots, N_m, \dots)$$

An alternative form of the fundamental relation:

$$U = U(S, V, N_1, \dots, N_m, \dots)$$



Possible because of the monotonic dependence of S on U

The two forms of the fundamental relation are called **entropy representation** $S(\dots)$ and **energy representation** $U(\dots)$ of the fundamental relation.

The Postulates

Equilibrium states of a macroscopic system are completely described by the values of its extensive coordinates ($U, V, N_1 \dots N_m, \dots$).

There exists a function of the extensive coordinates of a macroscopic system and its environment (called the entropy S) that is maximized by the equilibrium values of unconstrained extensive coordinates.

The entropy is extensive. It is a continuous, differentiable and monotonically increasing function of the internal energy.

$$S = 0 \text{ if } (\partial U / \partial S)_{V, N_1 \dots N_m} = 0.$$

+ the conservation of energy:

$$dU = \delta W + \delta Q$$

How do we find the fundamental relation?

1. In many cases one can derive the fundamental relation from a *set of simple experimental observations* that relate various thermodynamic parameters to each other (e.g., $PV = NRT$, etc. for ideal gas).

2. If we know details of the microscopic interactions between atoms and molecules of the system, we can calculate the fundamental relation by the methods of *statistical mechanics*.

Many general properties of macroscopic systems can be derived *without knowing the explicit functional form* of the fundamental relation!

Physical meaning of entropy: a detour to statistical physics

What is entropy? How do we calculate $S(U, V, N_1 \dots N_m, \dots)$?

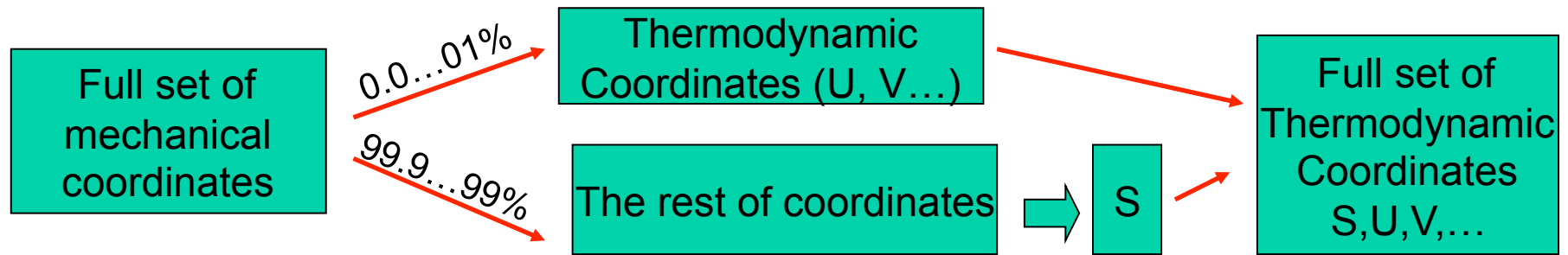
Statistical mechanics gives the answer.

Entropy is given by the logarithm of the number of accessible microscopic states of the system.

$$S = \text{const} * \ln(\Omega)$$

$\Omega(U, V, N_1 \dots N_m, \dots)$ = the number of microscopic realizations of the macroscopic state with given values of $U, V, N_1 \dots N_m, \dots$

From Mechanics to Thermodynamics



Remember that there is an enormous **number of microscopically distinct states** of a macroscopic thermodynamic system $\sim \exp(S)$.

Many of these microscopically different states **have the same macroscopic thermodynamics coordinates**. All coordinates other than the macroscopic ones are replaced with a **single new thermodynamic coordinate – entropy**.

This replacement of the majority of the degrees of freedom of a system with a single coordinate is the most enormous simplification in physics.

From Microscopic Coordinates to Entropy

What is the recipe for the transformation below?

The rest of coordinates $\Rightarrow$ S

- Each microscopic coordinate has a **phase space** associated with it.
- The number of possible states of this coordinate is proportional to its **phase space volume**
- There is also a phase space volume of a **set of coordinates**
- Entropy is **logarithm of the phase space volume of the microscopic coordinates of the system**
- Phase space volume depends on the macroscopic coordinates hence **$S(U, V, N_1 \dots N_m, \dots)$**

