CHM 421/621
Statistical Mechanics

Lecture 6 Postulates of Thermodynamics

Introduction and Review

Lecture Plan

Review of Thermodynamics

Basic Formalism

- Extensive variables and equilibrium states (Postulate 1)
- Fundamental question in thermodynamics
- Entropy function
- Postulates regarding entropy function (Postulate 2-4)

Conditions of Equilibrium

Equilibrium Relations

Legendre Transformed Representations

Stability of Thermodynamic Systems

Basic Formalism

Extensive Variables and Equilibrium States

Postulate 1

"There exist particular states (called equilibrium states) of simple systems that, macroscopically, are characterised completely by the internal energy U, the volume V, and the mole numbers $N_1, N_2, N_3,$ etc., of the chemical components."

- H. B. Callen

Motivated by the observation that there is a natural tendency for physical systems to move towards states where their macroscopic properties are static and independent of any perturbation they incurred in the past.

The values of the extensive parameters are presumed to be externally controllable and measurable.

Basic Formalism

Extensive Variables and Equilibrium States

<u>Connection to concept of microstates</u>?

The macroscopic equilibrium state is achieved by *rapid and incessant transitions* among all the microstates consistent with the given boundary conditions (extensive variables).

<u>What if the mechanism for transitions is not very effective</u>?
Then the system gets stuck in a small subset of microstates. E.g. glass, steel, etc.

The practical criterion for detecting an equilibrium state is verifying that the *properties of the state are consistently described by thermodynamic theory*.

Basic Formalism

Extensive Variables and Equilibrium States

Walls and constraints

Constraining V : Rigid walls (processes do not do any mechanical work)
Constraining N : Impermeable walls (no overall chemical composition change)

Controlling and measuring Internal Energy

E.g. Consider a container with ice and water. We can change ice into water by vigorous stirring. Thus, work done on the system can cause a state change.

Alternatively, if we keep the container at room temperature also ice melts yielding the same state. Thus, state change occurs due to heat transfer.

Clearly, U of the container has changed between the two states despite V and N remaining unchanged.

Basic Formalism

Extensive Variables and Equilibrium States

Controlling and measuring Internal Energy

$$Q = \Delta U - W$$ First law of thermodynamics

Internal energy can be controlled/changed by these two agencies (work/heat) by using appropriate walls.

Adiabatic walls => No heat flow =>$\Delta U = W$
(way to measure internal energy change)

Diathermal walls => Allows heat flow

Question: Can any two equilibrium states of a system be connected by an adiabatic mechanical process?

Basic Formalism

Extensive Variables and Equilibrium States

Direction of conversion?

In principle, any two equilibrium states (with the same mole numbers) can be connected using an adiabatic mechanical process. But, not necessarily in both directions (*Irreversibility* of a process).

Reversible process: A process which is sequence of equilibrium states only.

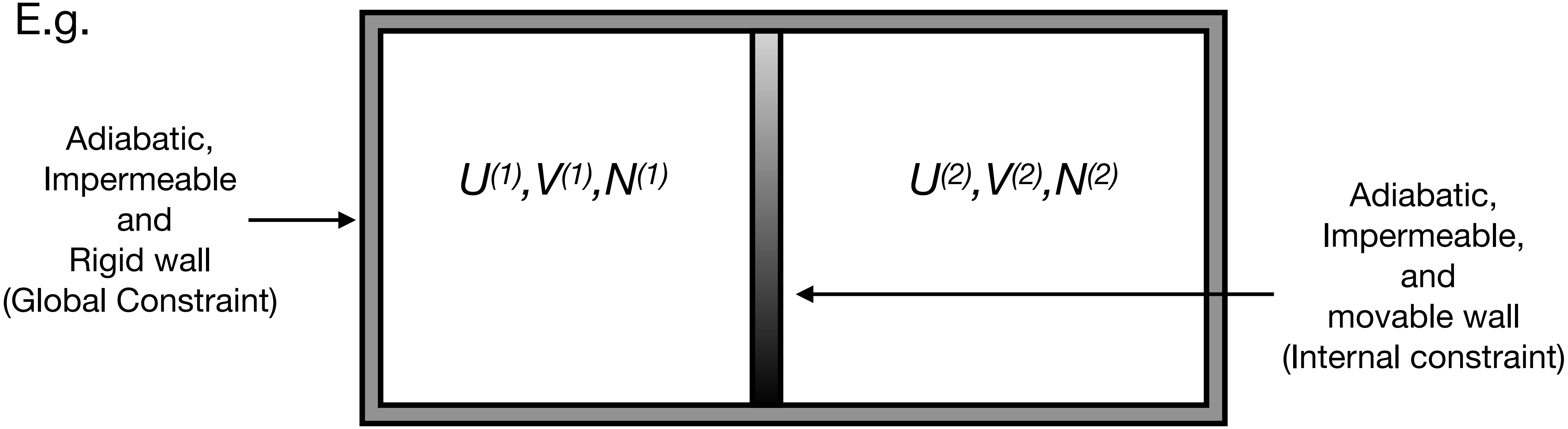
Practically, such processes are realised as quasi-static processes.
(Will discuss later)

Basic Formalism

Basic problem of thermodynamics

“The single all-encompassing problem of thermodynamics is the determination of the equilibrium states that eventually result after the removal of internal constraints in a closed, composite system.”

E.g.



When the internal wall is released, what will be its final position and the resulting internal energies in the two compartments?

Basic Formalism

Entropy Function

Postulate 2: 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 (removal) of an internal constraint are those that maximise the entropy over the manifold of constrained equilibrium states.

$$S \equiv S(U, V, N) \longrightarrow \text{Fundamental Relation}$$

At equilibrium, $dS = 0$

Also called the entropy maximisation postulate.

Basic Formalism

Postulates Regarding Entropy Function

Postulate 3: The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous, differentiable and a monotonically increasing function of the energy.

$$S = \sum_{\alpha} S^{(\alpha)}$$

Where $S^{(\alpha)} \equiv S^{(\alpha)}(U^{(\alpha)}, V^{(\alpha)}, N^{(\alpha)})$

Additivity property also implies that for a simple system the entropy is a homogenous function of the extensive parameters.

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$$

Basic Formalism

Postulates Regarding Entropy Function

Postulate 3: The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous, differentiable and a monotonically increasing function of the energy.

Monotonicity implies that

$$\boxed{\left(\frac{\partial S}{\partial U}\right)_{V,N} > 0}$$

This is an important requirement because, as it turns out, the reciprocal of this derivative will be the temperature of the system.

Basic Formalism

Postulates Regarding Entropy Function

Postulate 3: The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous, differentiable and a monotonically increasing function of the energy.

Continuity, differentiability and monotonicity imply that the entropy can be inverted w.r.t. the energy and that the latter is a single-valued, continuous, differentiable function of *S,V,N*.

i.e. $S \equiv S(U, V, N) \Rightarrow U \equiv U(S, V, N)$

Basic Formalism

Postulates Regarding Entropy Function

Postulate 3: The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous, differentiable and a monotonically increasing function of the energy.

Note that the extensivity of *S, U, V* allow us to scale the properties of a system of *N* moles from this of a system of 1 mole.

i.e. $$S(U,V,N) = N\ S(U/N,V/N,1) \equiv N\ s(u,v)$$

Molar quantities

Basic Formalism

Postulates Regarding Entropy Function

Postulate 4: The entropy of any system vanishes in the state for which

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = 0$$

The immediate implication is that unlike *U, S* has a uniquely defined zero.

Connections to third law of thermodynamics.