MME231: Lecture 13

Equilibrium in Thermodynamic Systems

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Today's Topics

- Intuitive meaning of equilibrium
  - Steady state vs. equilibrium state
  - Stable, unstable and metastable equilibria
  - Homogeneous vs. heterogeneous equilibria
- Thermodynamic formulation of the general conditions for equilibrium
- Mathematical formulation of the general conditions for equilibrium
- Alternate formulation for the criterion equilibrium

Intuitive Meaning of Equilibrium

A STATE OF REST

- The final resting point
- The condition is time independent

A STATE OF BALANCE

- The system will deviate from this position only due to an external influence to a new equilibrium state with respect to that external influence

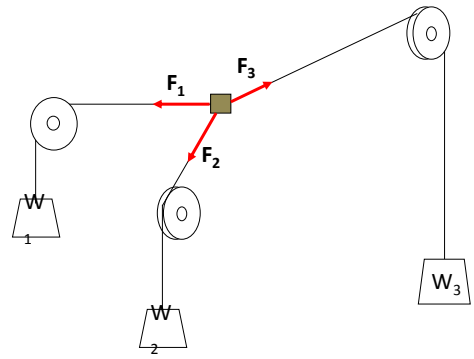

Fig. 5.1

- If the first condition is obeyed, but the second one isn't, then the system is in a **steady state** rather than in thermodynamic equilibrium.

Steady State vs. Equilibrium state

Example:

metal rod of which both ends are kept at different, constant temperatures

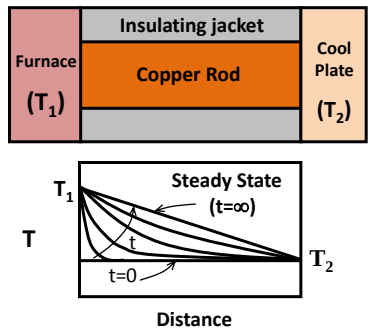

Fig. 5.2

- When attains a time invariant system, Isolate it from surroundings
- If system starts changing
  → **steady state**
- If no changes occur
  → **equilibrium state**

Classification of Equilibrium

Stable/True equilibria

- Any infinitesimal action will cause an infinitesimal but reversible change
- Change in direction of action will reverse the direction of change
- Withdrawal of the action will the original state of the system

Unstable/Labile equilibria

- Any infinitely small action will produce a finite/irreversible change

Metastable equilibria

- Not every infinitesimal action will cause an infinitesimal change
- There exists sufficiently small actions which produce a finite change
- Example: Supercooled liquid; Martensitic steel

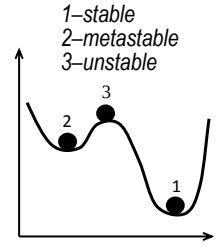

Fig. 5.3

Homogeneous vs. Heterogeneous equilibrium

The General Conditions for Equilibrium

Thermodynamic Formulation

- When two systems coming from two **different initial conditions** follow **two different processes** and attain the **same equilibrium state**, what will be the internal conditions of these two systems?

  Answer: Exactly the same.
  The approach of a system towards equilibrium is immaterial.

- All systems attaining **the same final equilibrium states** using different processes (open, isolated, adiabatic, isothermal etc.) will have the **same internal conditions**.

Entropy change for an isolated system

- No transfer/exchange of any kind with the surroundings.
- Entropy change will result entirely from entropy production.
- Which is, by Second Law, is always positive.

☐ This, in turn, leads to the **criterion for equilibrium**:

> **For an isolated system, the equilibrium state corresponds to the state with maximum entropy**

☐ This criterion is also an **extremum principle** and **applies only to an isolated system**

> **For an isolated system, the equilibrium state corresponds to the state with maximum entropy**

☐ Can this **criterion for equilibrium** which applies only to an **isolated system** be the **general** criterion for equilibrium

- that can be applied to any kind of system
- undergoing even if the most complex kind of processes

to determine the **conditions for equilibrium**?

☐ Can we generalize this statement to systems that are **not** isolated from their surroundings?

☐ Can there be **another state that has higher entropy** than the equilibrium state?

The General Conditions for Equilibrium

Mathematical Formulation

- Given a function (here S) of several variables and find the values of the set of variables that corresponds to an extreme value (here a maximum) of the function.
- The extremum principle also implies that there exist some parameters which are not independent.
- The extreme sought here, therefore, is a **constrained** maximum.

General strategy for finding a constrained maximum of entropy

1. Write a differential expression for the change in entropy.
2. Write differential expressions for the constraints.
3. Use the isolation constraints to eliminate dependent variables.
4. Set the coefficients of each of the differentials in the new expression of dS equal to zero.

The General Conditions for Phase Equilibrium

- A two-phase system consists of two phases (say, α and β), separated by **a phase boundary**.
- **Each phase has its own properties** (internal energy, entropy, volume, etc). For all these extensive properties, the total value for the system is the sum of the values for the parts (phases).
- Although the boundary of the overall system is isolated, the **boundary between phases is open**.

- Since matter and energy can flow freely between the phases, we need a generalized expression for the internal energy.

$$U'^{\alpha} = U'^{\alpha}(S'^{\alpha}, V'^{\alpha}, n'^{\alpha})$$

A prime (') symbol is given to extensive variables only

where n'^{α} is the number of moles in phase α.

- The combined statement of the first and second law becomes

$$dU'^{\alpha} = T^{\alpha} dS'^{\alpha} - P^{\alpha} dV'^{\alpha} + \mu^{\alpha} dn'^{\alpha}$$

where $\mu^{\alpha} = \left(\frac{\partial U'^{\alpha}}{\partial n'}\right)_{S'^{\alpha}, V'^{\alpha}}$

is the **chemical potential** of component making up phase α

$$dU'^{\alpha} = T^{\alpha} dS'^{\alpha} - P^{\alpha} dV'^{\alpha} + \mu^{\alpha} dn'^{\alpha}$$

- Rearranging the expression for dS'^{α} yields:

$$dS'^{\alpha} = \left(\frac{1}{T^{\alpha}}\right) dU'^{\alpha} + \left(\frac{P^{\alpha}}{T^{\alpha}}\right) dV'^{\alpha} - \left(\frac{\mu^{\alpha}}{T^{\alpha}}\right) dn'^{\alpha}$$

- Similarly for phase β:

$$dS'^{\alpha} = \left(\frac{1}{T^{\beta}}\right) dU'^{\beta} + \left(\frac{P^{\beta}}{T^{\beta}}\right) dV'^{\beta} - \left(\frac{\mu^{\beta}}{T^{\beta}}\right) dn'^{\beta}$$

- Since the total entropy of the system is simply the sum of the entropies of the phases, we find

$$S'_{sys} = S'^{\alpha} + S'^{\beta}$$

$$dS'_{sys} = d(S'^{\alpha} + S'^{\beta}) = dS'^{\alpha} + dS'^{\beta}$$

$$= \left(\frac{1}{T^{\alpha}}\right) dU'^{\alpha} + \left(\frac{P^{\alpha}}{T^{\alpha}}\right) dV'^{\alpha} - \left(\frac{\mu^{\alpha}}{T^{\alpha}}\right) dn'^{\alpha}$$

$$+ \left(\frac{1}{T^{\beta}}\right) dU'^{\beta} + \left(\frac{P^{\beta}}{T^{\beta}}\right) dV'^{\beta} - \left(\frac{\mu^{\beta}}{T^{\beta}}\right) dn'^{\beta}$$

- For an isolated system,

$$dU'_{sys} = d(U'^{\alpha} + U'^{\beta}) = dU'^{\alpha} + dU'^{\beta} = 0; \quad \mathbf{dU'^{\alpha} = -dU'^{\beta}}$$

$$dV'_{sys} = d(V'^{\alpha} + V'^{\beta}) = dV'^{\alpha} + dV'^{\beta} = 0; \quad \mathbf{dV'^{\alpha} = -dV'^{\beta}}$$

$$dn'_{sys} = d(n'^{\alpha} + n'^{\beta}) = dn'^{\alpha} + dn'^{\beta} = 0; \quad \mathbf{dn'^{\alpha} = -dn'^{\beta}}$$

- Using these equations to eliminate the dependent variables in dS'_{sys}

$$dS'_{sys,\,iso} = \left(\frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}}\right) dU'^{\alpha} + \left(\frac{P^{\alpha}}{T^{\alpha}} - \frac{P^{\alpha}}{T^{\beta}}\right) dV'^{\alpha} - \left(\frac{\mu^{\alpha}}{T^{\alpha}} - \frac{\mu^{\beta}}{T^{\beta}}\right) dn'^{\alpha}$$

- For equilibrium, $\mathbf{dS'_{sys,\,iso} = 0}$. This yields the conditions for equilibrium

$$\frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}} = 0 \qquad \mathbf{T^{\alpha} = T^{\beta}} \qquad \textbf{Thermal Equilibrium}$$

$$\frac{P^{\alpha}}{T^{\alpha}} - \frac{P^{\alpha}}{T^{\beta}} = 0 \qquad \mathbf{P^{\alpha} = P^{\beta}} \qquad \textbf{Mechanical Equilibrium}$$

$$\frac{\mu^{\alpha}}{T^{\alpha}} - \frac{\mu^{\beta}}{T^{\beta}} = 0 \qquad \boldsymbol{\mu^{\alpha} = \mu^{\beta}} \qquad \textbf{Chemical Equilibrium}$$

- Recall that these conditions are now valid for **general** one-component (unary) two-phase systems for any process

Thus a system will be in equilibrium if all of its components are in thermal, mechanical and chemical equilibrium with each other

Alternate Formulation for the Criterion for Equilibrium

1. For systems constrained to constant entropy, volume, and quantity of its components, the **internal energy** decreases, and is a **minimum** at equilibrium.
2. For systems constrained to constant entropy, pressure, and quantity of its components, the **enthalpy** decreases, and is a **minimum** at equilibrium.
3. For systems constrained to constant temperature, volume, and quantity of its components, the **Helmholtz free energy** decreases, and is a **minimum** at equilibrium.
4. For systems constrained to constant temperature, pressure, and quantity of its components, the **Gibbs free energy** decreases, and is a **minimum** at equilibrium.

Next Class

Lecture 14-15
Review Classes