MME 231: Lecture 03

The Structure of Thermodynamics

Thermodynamic Processes and Relations

A. K. M. B. Rashid
Professor, Department of MME
BUET, Dhaka

Today's Topics

- Thermodynamic Processes
- Thermodynamic Relations
- Problem Solving

Thermodynamic Processes

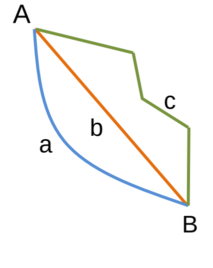
- A **process** suggests
  - ❶ change in system from one state to another
  - ❷ some operations by which the change is achieved

- A **path** represents a sequence of situations a system passes through during a change in the state of the system.

Process $A \Rightarrow B$

System changes from state A to state B;

But **does not indicate** any particular operation or the path it followed



Three different paths a, b, c for the process $A \rightarrow B$

A process is often specified with certain **constraints** imposed on the system and/or its surroundings.

Classification of Processes

Adiabatic Process

- **No heat transfer** occurs across the boundary between the system and its surroundings
  - If the temperature gradient, $\Delta T = 0$, no heat will transfer
  - If $\Delta T \neq 0$, heat will transfer (which is a rate process) so for a short period of time, the process can be assumed to be adiabatic (e.g., compression of air and gasoline in internal combustion engine)
- How to recognise an adiabatic process?
  - Process is carried out quickly
  - Well insulated boundary

Isothermal Process

- **Temperature is uniform** at every point throughout the system and remains constant during the entire process
  - If $\Delta T = 0$, Transfer of heat = 0.
  - If $\Delta T \neq 0$, Transfer of heat/work will occur until $\Delta T = 0$.
- If the process produces heat
  - Transfer of heat and/or work across the boundary is mandatory
  - Process should occur for a prolonged period of time to encourage heat transfer
- How to recognise an adiabatic process?
  - Process is carried out very slowly (close to infinity)
  - Permeable boundary

Isobaric Process

- **Pressure remained constant** throughout the system.

Isochoric Process

- **Volume remained constant** throughout the system.
- **Impermeable** and **rigid** container/boundary

Cyclic Process

- The initial and final states of the system are the **same**.
- The overall changes in all state variables are **zero**.

$$\oint dZ = 0$$

- If the cyclic change in a state of a system results a **ZERO** change in a property, that property is a state function

Table 2.1:
Characteristics of different thermodynamic processes

Process	Constraints imposed	Quantity exchanged
Isobaric	Pressure remains constant ($\Delta P=0$)	Heat and work may be exchanged
Isothermal	Temperature remains constant ($\Delta T=0$)	Heat and work may be exchanged
Isochoric	Volume remains constant ($\Delta V=0$)	Only heat is exchanged
Adiabatic	System remains insulated ($Q=0$)	Only work is exchanged

Thermodynamic Relations

1. Laws of Thermodynamics

- These fundamental equations form the basis of all thermodynamic relations.
- Generally describes the connection between the different forms of energy and state variables.

2. Definitions

- There are quite a few number of thermodynamic properties that are defined in terms of previously formulated quantities.
- They describe a particular class of system or process.
- In this category, there are some energy function and some experimental variables.

3. Coefficient Relations

$$Z = Z(X, Y)$$

$$dZ = \left(\frac{\partial Z}{\partial X}\right)_Y dX + \left(\frac{\partial Z}{\partial Y}\right)_X dY \qquad (2.2)$$

$$dZ = M\,dX + N\,dY \qquad (2.3)$$

$$M = \left(\frac{\partial Z}{\partial X}\right)_Y \quad \text{and} \quad N = \left(\frac{\partial Z}{\partial Y}\right)_X \qquad (2.4)$$

Equations (2.4) are known as the coefficient relations.

4. Maxwell Relations

$$dZ = M\,dX + N\,dY \qquad (2.3)$$

$$M = \left(\frac{\partial Z}{\partial X}\right)_Y \quad \text{and} \quad N = \left(\frac{\partial Z}{\partial Y}\right)_X \qquad (2.4)$$

$$\left(\frac{\partial M}{\partial Y}\right)_X = \left[\frac{\partial}{\partial Y}\left(\frac{\partial Z}{\partial X}\right)_Y\right]_X = \frac{\partial^2 Z}{\partial X\,\partial Y}$$

$$\left(\frac{\partial N}{\partial X}\right)_Y = \left[\frac{\partial}{\partial X}\left(\frac{\partial Z}{\partial Y}\right)_X\right]_Y = \frac{\partial^2 Z}{\partial X\,\partial Y}$$

$$\left(\frac{\partial M}{\partial Y}\right)_X = \left(\frac{\partial N}{\partial X}\right)_Y \qquad (2.5)$$

If a function Z = Z (X, Y) obeys the Maxwell relation, the function will be a state variable.

Equation (2.5) is known as the Maxwell relation.

5. Condition for Equilibrium

- When an external force is acted upon a system, the system undergoes changes until it has exhausted all of its capacity for change.
- When the system attains this final resting place, we indicate that the system is in **equilibrium** with its surroundings.
- The **conditions for equilibrium** are a set of equations that describe the relationships between state functions that must exist within the system when it attains the equilibrium (or stable) state.

Problem Solving

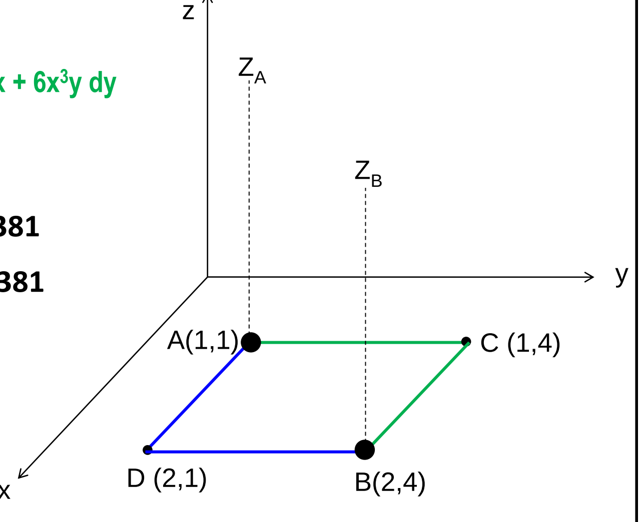
Example 2.1

Is the function $z = 9x^2y^2\,dx + 6x^3y\,dy$ an exact differential ?

$\Delta Z = \Delta Z_{CA} + \Delta Z_{BC} = 381$

$\Delta Z = \Delta Z_{DA} + \Delta Z_{BD} = 381$

$\Delta Z = \Delta Z_{BCA} = \Delta Z_{BDA}$



Thus the function z is an exact differential.

Problem 2.15

Write total differential equation of the function

$z = 17x^4y + 22xy^5$

and then, using Maxwell relation, prove that z is a state function.

$$dZ = \left\{17\left(4x^3\right)y + 22y^5\right\}dx + \left\{17x^4 + 22\left(5y^4\right)\right\}dy$$

$$M = 68x^3y + 22y^5 \quad ; \quad N = 17x^4 + 110y^4$$

$$\left(\frac{\partial M}{\partial y}\right)_x = 68x^3 + 110y^4$$

$$\left(\frac{\partial N}{\partial x}\right)_y = 68x^3 + 110y^4$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Thus, z is a state function.

Next Class

Lecture 04

The First Law of Thermodynamics

Rashid/ Ch#3 – Sec. 3.1