What is Thermodynamics?
"A law is more impressive the greater the simplicity of its premises, the more different are the kinds of things it relates, and the more extended its range of applicability. Therefore, the deep impression which classical thermodynamics made on me. It is the only physical theory of universal content which I am convinced, that within the framework of applicability of it basic concepts will never be overthrown."

Albert Einstein

Thermodynamics

- Classical
- Statistical
- Kinetic Theory

The description of a physical system

- Macroscopic
- Microscopic
Classical Thermodynamics
- Macroscopic approach
- General properties of the system
- Macroscopic variables

Statistical Thermodynamics
- Microscopic approach
- Specific properties of the system
- Microscopic variables

Kinetic Theory
- Microscopic approach
- Specific properties of the system
- Microscopic variables
Physical System
- Microscopic model
- Experiment

Method
- Mechanics
- Statistics

Thermodynamic System
- consists of very large number of particles
- has the boundary
- has the surroundings
Thermodynamic system

The part of the universe treated at a given problem, which state can be completely determined by given thermodynamic variables.

Macroscopic approach

- Treats system as a whole
- Macroscopic variables

Microscopic approach

- Treats system as collection of particles
- Microscopic variables
Thermodynamic variables
- Extensive
- Intensive

Thermodynamic State
- Thermodynamic variables are well defined for all volume elements of the system large enough that macroscopic description can be applied
- Thermodynamic variables are not changing with time
Thermodynamic state

- Macrostate
- Microstate

Interaction between the system and its environment

Equilibrium

- Mechanical
- Thermal
- Chemical
Temperature

An Illustration of the Zeroth Law of Thermodynamics

Thermal Equilibrium

No heat flows (A is in equilibrium with B)

No heat flows (C is in equilibrium with B)

No heat flows (A and C are found to be in equilibrium)
Zero Law of Thermodynamics

Two or more systems in mutual thermal equilibrium—that is, with no tendency of heat to flow through the conducting walls connecting them all have the same temperature. Or when two systems are in thermal equilibrium with the third system, they are in thermal equilibrium with each other and all the three systems have the same temperature.

Equation of State and Existence of Temperature

Empirical Temperature and Thermometers
A Constant-Volume Gas Thermometer

\[ \theta = Cp \]

Temperature Scales
Reference points of Kelvin Scale

- Absolute zero
- Triple point of water \( \theta_s = 273.16 \, K \)

Ideal Gas Thermometer

\[
\theta_j = \frac{Cp_j}{3}
\]

\[
\theta = 273.16 \, K \frac{P}{p_3}
\]

\[
T = 273.16 \, K \lim_{p_1 \to 0} \left( \frac{p}{p_3} \right)_V
\]

Determining Absolute Zero
Celsius and Fahrenheit Scales

\[ t_C = T - 273.15^\circ \]

\[ t_F = \frac{9}{5} t_C + 32^\circ \]

Thermodynamic Process

Heat Transfer
Insulating (adiabatic) wall
Thermally conducting (diathermic) wall

\[ \delta W = Fdx \]
Work done by gas in a cylinder

\[ \delta W = pdV \]

**Sign Convention**
- Work is positive if it is done by the system
- Work is negative if it is done on the system

**Work**
- Differential of work is inexact differential
- Is not function of state
- Depends on the process
Work done by gas in the cylinder

Work done by a gas in the container

\[ W = \int Fdx = \int pdV \]

Work done by a gas in the container over a cycle
Work done in adiabatic process does not depend on the choice of the path

Internal Energy

\[ U_2 - U_1 = -W_{ad} = - \int_{ad} F \, dx \]

The First Law of Thermodynamics

\[ dU = \delta Q - \delta W \]
\[ U_2 - U_1 = Q - W \]
The First Law of Thermodynamics

When a system changes from an initial state 1 to a final state 2, the sum of work $W$ and the heat $Q$, which it receives from surroundings is determined by the states 1 and 2, it does not depend on the intermediate process.

Thermodynamic Process

- Reversible
- Irreversible
Reversible process

If the system under consideration changes from original state 1 to final state 2 and its environment changes from state a to state b, then in some way it is possible to return the system from 2 to 1 and in the same time return the environment from b to a, the process (1,a) to (2,b) is said to be reversible.

Heat Transfer and Work

Heat Engine
- produces useful work
- works through a cycle
- exchanges heat with environment
Carnot Cycle for Ideal Gas

The Second Law of Thermodynamics

Experimental Evidence of the Second Law of Thermodynamics
Caratheodory's principle:

For a given thermodynamic state of thermally uniform system, there exists another state which is arbitrarily close to it but can not be reached from it by an adiabatic change.

Theorem of Caratheodory

If differential form \( M(x, y, ...) \, dx + N(x, y, ...) \, dy + ... \) has a property that in the space of its variables every arbitrary neighborhood of point P contains other points which are inaccessible from P along a path corresponding to the solution of its differential equation, then an integrating denominator for the expression exists.

Clausius' principle

A process which involves no change other than the transfer of heat from a hotter to a cooler body is irreversible, or it is impossible for heat to transfer spontaneously from a colder to hotter body without causing other changes.
Thomson’s (Kelvin’s) principle:

A process in which work is transformed into heat without any other changes, is irreversible; or, it is impossible to convert all the heat taken from a body of uniform temperature into work without causing other changes.

Principle of the impossibility of the a perpetuum mobile of the second kind

It is impossible to devise an engine operating in a cycle which does work by taking heat from a single heat reservoir without producing any other change.

General Carnot Cycle

- Two isothermal and two adiabatic processes
- Efficiency \( \eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \)
Carnot’s Principle

The efficiency of a reversible Carnot cycle operating between heat reservoirs $R_1$ and $R_2$ is uniquely determined by the temperatures of the heat reservoirs and the efficiency of any irreversible Carnot cycle operating between the same heat reservoirs is less than the efficiency of reversible Carnot engine

$$\eta' \leq \eta = 1 - \frac{T_2}{T_1}$$

Reversible Carnot Cycle

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2},$$

$$T = 273.16K \left| \frac{Q}{Q_3} \right|$$

Clausius’s inequality for arbitrary cycle

When a system performs a cycle while in contact with environment and absorbs heat from the environment at temperature $T$, then the following holds

$$\oint \frac{\delta Q}{T} \leq 0$$
Entropy

\[ S = \int_{1}^{\text{reversible}} \frac{\delta Q}{T}, \]
\[ dS = \frac{\delta Q}{T} \]

Entropy is an extensive variable

Second Law of Thermodynamics

\[ \int_{1}^{2} \frac{\delta Q}{T} \leq \Delta S, \]
\[ \frac{\delta Q}{T} \leq dS \]
Third Law of Thermodynamics

If one tries to reduce the temperature to absolute zero by repeating the series of operations, each successive operation yields a smaller change of temperature and it appears that $T=0$ will never be reached.

Nernst-Simon Theorem

$\Delta S \to 0, \ T \to 0$

Infinitesimal Reversible Process in the closed system

\[ dU = \delta Q - \delta W, \]
\[ dU = TdS - pdV \]
Infinitesimal Reversible Process in the open multi-component system

- Chemical potential
  \[ \mu_i \equiv \left( \frac{\partial U}{\partial N_i} \right)_{S,V,N,N_m} \]

\[ dU = TdS - pdV + \sum_i \mu_i dN_i \]

Other Thermodynamic Functions

- Enthalpy \( H \equiv E + pV \)
- Helmholtz free energy \( F \equiv E - TS \)
- Gibbs free energy \( G \equiv E + pV - TS \)
- Grand potential \( \Omega \equiv F - \mu N \)

Differentials of thermodynamic potentials

\[ dH = TdS + Vdp + \sum_i \mu_i dN_i, \]
\[ dF = -SdT - pdV + \sum_i \mu_i dN_i, \]
\[ dG = -SdT + Vdp + \sum_i \mu_i dN_i \]
\[ d\Omega = -SdT - pdV - \sum_i N_i d\mu_i, \]
\[ G = \sum_{i} \mu_i N_i \]

**Gibbs-Duhem Relation**

\[ SdT - Vdp + Nd\mu = 0 \]

**Criteria for Equilibrium**

\[ \delta Q \leq TdS, \]
\[ dU + pdV \leq TdS, \]
\[ dU + pdV - TdS \leq 0 \]
Isolated System
- $dE=0$, $dV=0$, $dN=0$

$$dS \geq 0$$
- S has its maximum at equilibrium

The closed Isothermal system
- $dT=0$, $dN=0$, $dV=0$

$$dF \leq 0,$$
- F has its minimum at equilibrium

The closed Isobaric system
- $dT=0$, $dN=0$, $dp=0$

$$dG \leq 0,$$
- G has its minimum at equilibrium
The open Isothermal system

- $dT=0$, $d\mu=0$, $dV=0$

\[ d\Omega \leq 0, \; \Omega = -pV \]

- $\Omega$ has its minimum at equilibrium

First Partial differential coefficients of thermodynamic potentials

Measurable Properties of the system

- The coefficient of volume thermal expansion
  \[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_x \]

- Compressibility
  \[ \kappa = \frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_x \]
Heat Capacity

- at constant volume
  \[ C_v = \left( \frac{\delta Q}{\delta T} \right)_v = \left( \frac{\partial U}{\partial T} \right)_v = T \left( \frac{\partial S}{\partial T} \right)_v \]

- at constant pressure
  \[ C_p = \left( \frac{\delta Q}{\delta T} \right)_p = \left( \frac{\partial H}{\partial T} \right)_p = T \left( \frac{\partial S}{\partial T} \right)_p \]

The Cross-Differentiation Identity

\[ \frac{\partial}{\partial x} \left( \frac{\partial W}{\partial y} \right) = \frac{\partial}{\partial y} \left( \frac{\partial W}{\partial x} \right) = \frac{\partial^2 W}{\partial x \partial y} = \frac{\partial^2 W}{\partial y \partial x} \]

\[ \left( \frac{\partial p}{\partial T} \right)_v = \frac{1}{T} \left\{ \left( \frac{\partial U}{\partial V} \right)_T + p \right\} \]

\[ \left( \frac{\partial V}{\partial T} \right)_p = -\frac{1}{T} \left\{ \left( \frac{\partial H}{\partial p} \right)_T - V \right\} \]
Maxwell’s Relations

\[ \left( \frac{\partial S}{\partial p} \right)_V = -\left( \frac{\partial V}{\partial T} \right)_S \]
\[ \left( \frac{\partial S}{\partial V} \right)_p = \left( \frac{\partial p}{\partial T} \right)_S \]
\[ \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial p}{\partial T} \right)_V \]
\[ \left( \frac{\partial S}{\partial p} \right)_T = -\left( \frac{\partial V}{\partial T} \right)_p \]

Example

Show that internal energy of a material whose equation of state has the form \( p = f(V)T \) is independent of the volume.