Thermodynamics

- Classical
- Statistical
- Kinetic Theory

Classical Thermodynamics

- Macroscopic approach
- General properties of the system
- Macroscopic variables
An Illustration of the Zeroth Law of Thermodynamics

- 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)

Temperature Scales

Thermodynamic Process
Heat Transfer

- Insulating (adiabatic) wall
- Thermally conducting (diathermic) wall

Work
Work

\[ \delta W = F \, dx \]

Work done by gas in a cylinder

\[ \delta W = p \, dV \]

Work

- differential of work is inexact differential
- is not function of state
- depends on the process
Work done by gas in the cylinder

\[ W = \int F \, dx = \int p \, dV \]
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 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 cannot be reached from it by an adiabatic change.
Theorem of Caratheodory

If differential form \( M(x,y,...) \, dx + N(x,y,...) \, dy \pm \) 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 \( R1 \) and \( R2 \) 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

\[ \frac{Q_1}{T_1} = \frac{Q_2}{T_2}, \]

\[ T = 273.16 K \frac{Q}{Q_3} \]

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

\[ S = \int_{1}^{rev} \frac{\delta Q}{T}, \]

\[ dS = \frac{\delta Q}{T} \]
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

\[ \Delta S \rightarrow 0, \; T \rightarrow 0 \]
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
  \[ \mu_i \equiv \left( \frac{\partial U}{\partial N_i} \right)_{S,V,N_{jn}} \]

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

Other Thermodynamic Functions

- Enthalpy
  \[ H \equiv U + pV \]

- Helmholtz free energy
  \[ F \equiv U - TS \]

- Gibbs free energy
  \[ G \equiv U + pV - TS \]

- Grand potential
  \[ \Omega \equiv F - \mu N \]
Differentials of thermodynamic potentials

\[ \begin{align*}
    dH &= TdS + Vdp + \sum_i \mu_i dN_i, \\
    dF &= -SdT - pdV + \sum_i \mu_i dN_i, \\
    dG &= -SdT + Vdp + \sum_i \mu_i dN_i, \\
    d\Omega &= -SdT - pdV - \sum_i N_i d\mu_i,
\end{align*} \]

Criteria for Equilibrium

\[ \begin{align*}
    \delta Q &\leq TdS, \\
    dU + pdV &\leq TdS, \\
    dU + pdV - TdS &\leq 0
\end{align*} \]

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
  \[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_V \]
- Compressibility
  \[ \kappa = \frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_V \]

Heat Capacity

- at constant volume
  \[ C_V = \left( \frac{\delta Q}{dT} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V \]
- at constant pressure
  \[ C_p = \left( \frac{\delta Q}{dT} \right)_p = \left( \frac{\partial H}{\partial T} \right)_p = T \left( \frac{\partial S}{\partial T} \right)_p \]
The Cross-Differentiation Identity

\[
\frac{\partial}{\partial x} \left( \frac{\partial W}{\partial y} \right) = \frac{\partial}{\partial y} \left( \frac{\partial W}{\partial x} \right) = \frac{\partial^3 W}{\partial x \partial y \partial x} = \frac{\partial^3 W}{\partial y \partial x \partial x}
\]

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

\[
\left( \frac{\partial V}{\partial T} \right)_p = -\frac{1}{T} \left( \frac{\partial H}{\partial p} \right)_T - V
\]

Maxwell’s Relations

\[
\left( \frac{\partial S}{\partial V} \right)_p = -\left( \frac{\partial V}{\partial T} \right)_s,
\]

\[
\left( \frac{\partial S}{\partial V} \right)_p = \left( \frac{\partial p}{\partial T} \right)_s,
\]

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

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

**Random Walk Problem**

Probability of taking $N$ steps with $n_1$ steps to the right and $n_2=N-n_1$ to the left

$$W_N (n_1) = \frac{N!}{n_1! n_2!} p^{n_1} q^{n_2}$$
\[ P_n(m) = \frac{N!}{\binom{N+m}{2} \binom{N-m}{2}} p^{\frac{N+m}{2}} (1-p)^{\frac{N-m}{2}} \]

The mean value of discrete variable

\[ \bar{u} = \frac{\sum_{i=1}^{M} P(u_i) u_i}{\sum_{i=1}^{M} P(u_i)} \]

\[ \bar{f}(u) = \sum_{i=1}^{M} P(u_i) f(u_i) \]
Moments of the distribution

Random walk problem calculations

Probability distribution for large N
Gaussian Distribution

\[
W(n_i) = \left[ 2\pi(\Delta n_i)^2 \right]^{-1/2} \exp\left[ -\frac{(n_i - \bar{n}_i)^2}{2(\Delta n_i)^2} \right].
\]

\[
W(n_i) = [2\pi Npq]^{1/2} \exp\left[ -\frac{(n_i - Np)^2}{2Npq} \right]
\]

Gaussian Distribution

\[
P(m) = [2\pi Npq]^{1/2} \exp\left[ -\frac{(m - N(p - q))^2}{8Npq} \right]
\]

Gaussian Distribution

\[
\mathcal{P}(x)dx = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[ -\frac{(x - \mu)^2}{2\sigma^2} \right]dx,
\]

\[\mu \equiv (p - q)Nl,\]

\[\sigma = 2\sqrt{Npq}l\]