

Lecture Notes on Thermodynamics

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Chapter 1

The Zeroth Law of Thermodynamics

1.1 Statement

✓ 0th Law

If two systems, A and B, are separately in equilibrium with a third system, C, then they are also in equilibrium with one another.

Despite its apparent simplicity, the zeroth law has the consequence of implying the existence of an important state function, the **empirical temperature** Θ , such that systems in equilibrium are at the same temperature.

1.2 Mathematical Formulation

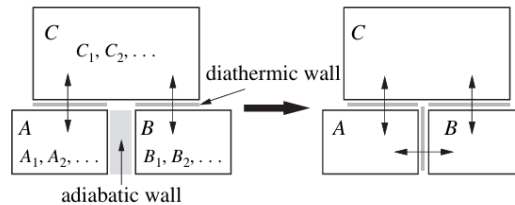


Figure 1.1: 0th Law, thermal Equilibrium

Let the equilibrium state of systems A , B , and C be described by the Parameter set $\{A_1, A_2, \dots\}$, $\{B_1, B_2, \dots\}$, and $\{C_1, C_2, \dots\}$, respectively.

If A and C are in equilibrium implies a constraint between the coordinates of A and C . Denote this constraint by:

$$f_{AC}(A_1, A_2, \dots; C_1, C_2, \dots) = 0 \quad (1.1)$$

The equilibrium of B and C implies a similar constraint:

$$f_{BC}(B_1, B_2, \dots; C_1, C_2, \dots) = 0 \quad (1.2)$$

We can solve each of the above equations for the coordinate C_1 to yield:

$$C_1 = F_{AC}(A_1, A_2, \dots; C_2, \dots) \quad (1.3)$$

$$C_1 = F_{BC}(B_1, B_2, \dots; C_2, \dots) \quad (1.4)$$

Thus, if C is separately in equilibrium with A and B , we must have:

$$F_{AC}(A_1, A_2, \dots; C_2, \dots) = F_{BC}(B_1, B_2, \dots; C_2, \dots) \quad (1.5)$$

According to the zeroth law, there is also equilibrium between A and B , implying the constraint $f_{AB}(A_1, A_2, \dots; B_1, B_2, \dots) = 0$. This implies that it must be possible to simplify the previous equality by canceling the coordinates of C . This reduces the condition for equilibrium of A and B to:

$$\Theta_A(A_1, A_2, \dots) = \Theta_B(B_1, B_2, \dots) \quad (1.6)$$

Equilibrium is characterized by a function Θ of thermodynamic coordinates. This function specifies the *equation of state*, and *isotherms* of A are described by the condition $\Theta_A(A_1, A_2, \dots) = \Theta$.

1.3 An example of Equilibrium Constraints

We need two systems in equilibrium. For simplicity we Consider two aspects of a system (A) a paramagnetic gas of magnetization M in a magnetic field B , and (B) the same gas of volume V at pressure P .

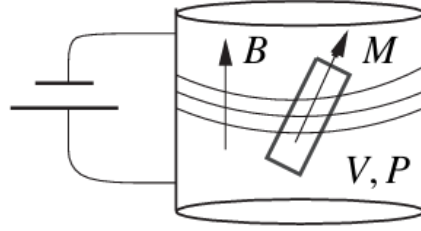


Figure 1.2: paramagnetic van der waals gas

In this system, we observe the following empirical relation similar to 1.6:

$$\frac{1}{N} \left(P + \frac{a}{V^2} \right) (V - b) \propto \frac{NB}{M} \quad (1.7)$$

this proportionality gives a constant. (Let us choose the constants that gives an easy form of the Actual Temperature)

$$\frac{1}{Nk_B} \left(P + \frac{a}{V^2} \right) (V - b) = \frac{N\mu_B^2 B}{3k_B M} = \Theta \quad (1.8)$$

These reproduce two well-known equations of state:

$$\begin{cases} (P + a/V^2)(V - b) = Nk_B T & \text{(van der Waals gas)} \\ M = (N\mu_B^2 B)/(3k_B T) & \text{(Curie paramagnet)} \end{cases} \quad (1.9)$$

where T represents the Kelvin temperature scale constructed using $\Theta = T(K)$.

Chapter 2

Ideal Gas

2.1 Introduction

An ideal gas has the following properties.

- The molecules of an ideal gas are point masses with negligible volume.
- There are no intermolecular forces between the gas molecules.
- Collisions between molecules and with the walls of the container are perfectly elastic.

2.2 Ideal Gas Laws

The behavior of an ideal gas is described by the following fundamental gas laws.

Boyle's Law

At constant temperature, the pressure of a given mass of gas is inversely proportional to its volume:

$$P \propto \frac{1}{V} \quad (T = \text{constant})$$

or

$$PV = \text{constant} \quad (2.1)$$

Charles's Law

At constant pressure, the volume of a given mass of gas is directly proportional to its absolute temperature:

$$V \propto T \quad (P = \text{constant})$$

or

$$\frac{V}{T} = \text{constant} \quad (2.2)$$

Gay–Lussac’s Law

At constant volume, the pressure of a given mass of gas is directly proportional to its absolute temperature:

$$P \propto T \quad (V = \text{constant})$$

or

$$\frac{P}{T} = \text{constant} \quad (2.3)$$

Avogadro’s Law

At constant temperature and pressure, the volume of a gas is directly proportional to the number of moles of the gas:

$$V \propto n \quad (T, P = \text{constant})$$

or

$$\frac{V}{n} = \text{constant} \quad (2.4)$$

This law implies that equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules. As a consequence, one mole of any ideal gas occupies a volume of 22.4 L at standard temperature and pressure (STP).

2.3 Ideal Gas Equation

Above mentioned gas laws implies the following proportionality:

$$PV \propto nT \quad (2.5)$$

This gives **macroscopic equation of state** for an ideal gas is

$$\boxed{PV = nRT} \quad (2.6)$$

where R is a proportionality constant. its called the universal gas constant.

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

Fundamental Constant

The number of constituent particles in one mole of any substance is defined as **Avogadro’s Number** (N_A):

$$\boxed{N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}}$$

Hence Total number of molecules of the gas of n mole is:

$$N = nN_A \quad (2.7)$$

Ideal gas equation reduces to:

$$PV = \frac{N}{N_A} RT$$

The quantity

$$\frac{R}{N_A} = k_B = 1.380649 \times 10^{-23} \text{ J K}^{-1} \quad (2.8)$$

is defined as the Boltzmann constant.

Thus, the ideal gas equation can be written in its **microscopic form** as

$$\boxed{PV = Nk_B T} \quad (2.9)$$

This form of the ideal gas equation relates macroscopic thermodynamic variables to microscopic molecular properties.

It leads to another form of ideal gas equation:

$$\boxed{P = \bar{n} k_B T} \quad (2.10)$$

where $\bar{n} = \frac{N}{V}$: Number density of the molecules in the system.

2.4 Work Done By an Ideal Gas

To understand the energy transfer in a thermodynamic process, we examine a gas filled inside a cylinder equipped with a movable piston.

Pressure is defined as the force acting per unit area:

$$P = \frac{F}{A} \implies F = P \cdot A \quad (2.11)$$

When an external force \vec{F} is applied to the piston, causing it to move by an infinitesimal displacement $d\vec{l}$, the work done is:

$$\delta W = \vec{F} \cdot d\vec{l} \quad (2.12)$$

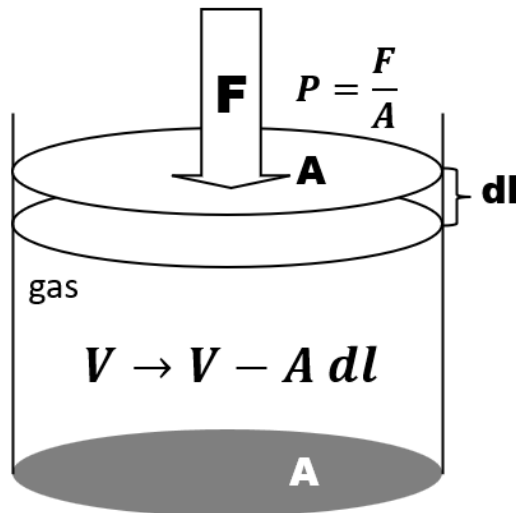


Figure 2.1: Cylinder-piston system: The gas is being compressed by an external force F .

2.4.1 Work Done by the External Agent

Substituting the force relation into the work equation, where the displacement dl occurs over the cross-sectional area A :

$$\delta W = (P \cdot A)dl \quad (2.13)$$

Since the change in volume is $dV = A \cdot dl$, the work done **by the external force on the system** is:

$$\delta W_{ext} = +P dV \quad (2.14)$$

2.4.2 System Perspective (Work Done by the Gas)

From the system's (the gas) point of view, if it is being compressed, the volume is decreasing. In physics, we often define work based on the system's action.

If the system is being worked upon (compressed), it is "doing" negative work because the displacement is opposite to the direction of the internal gas pressure.

Sign Convention for your Notes

- **Compression** ($dV < 0$):
Work done *by the gas* $\delta W = PdV$ is negative ($dW < 0$).
- **Expansion** ($dV > 0$):
Work done *by the gas* $\delta W = PdV$ is positive ($dW > 0$).

2.4.3 Total Work Done

For a finite change in volume from V_1 to V_2 , the total work done by the gas is obtained by integration:

$$W = \int_{V_1}^{V_2} P dV \quad (2.15)$$

This expression is valid for quasi-static thermodynamic processes, where the system remains in equilibrium at every stage.

Isothermal Process

For an isothermal process ($T = \text{constant}$) of an ideal gas ($PV = nRT$),

The work done by the gas is given by

$$W = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln \left(\frac{V_2}{V_1} \right) \quad (2.16)$$

Adiabatic Process

In an adiabatic process, (no heat is exchanged with the surroundings $\Delta Q = 0$). The equation of state is

$$PV^\gamma = \text{constant}$$

where $\gamma = \frac{C_P}{C_V}$. The work done is

$$W = \int_{V_1}^{V_2} \frac{K}{V^\gamma} dV = \frac{KV_1^{-\gamma}V_1 - KV_2^{-\gamma}V_2}{\gamma - 1} = \frac{P_1V_1 - P_2V_2}{\gamma - 1} \quad (2.17)$$

In this process, the work done comes at the expense of internal energy.

Isochoric Process

In an isochoric ($V = \text{constant}$) process,

$$dV = 0$$

Hence, the work done is

$$W = \int P dV = 0$$

No mechanical work is done, and any heat supplied changes only the internal energy.

Isobaric Process

In an isobaric process ($P = \text{constant}$), The work done is

$$W = \int_{V_1}^{V_2} P dV = P(V_2 - V_1) \quad (2.18)$$

Using the ideal gas equation ($PV = nRT$), this can also be written as

$$W = nR(T_2 - T_1) \quad (2.19)$$

Cyclic Process

In a cyclic process, the system returns to its initial state. The work done over one complete cycle is

$$W = \oint P dV$$

and is equal to the area enclosed by the cycle on the P - V diagram.

Free Expansion

In free expansion, the gas expands into a vacuum.

$$P_{\text{external}} = 0$$

Hence, the work done is

$$W = 0$$

No work is done despite the increase in volume.

Problem 2.1. polytropic process

calculate work done by the gas following the polytropic path: $PV^x = C$ where C is a constant.

2.5 Kinetic Theory of Ideal Gases

The Kinetic Theory of Gases provides a microscopic explanation for macroscopic properties like pressure and temperature. It treats a gas as a collection of a large number of molecules in constant, random motion.

Consider an ideal gas consisting of N molecules, each of mass m , enclosed in a cubical container of side L . The volume of the container is $V = L^3$.

Momentum Change per Collision

Suppose a molecule moves with velocity $\vec{v} = (v_x, v_y, v_z)$. When it collides elastically with the wall perpendicular to the x-axis, its velocity component v_x reverses to $-v_x$. The change in momentum (Δp_x) is:

$$\Delta p_x = (-mv_x) - (mv_x) = -2mv_x \quad (2.20)$$

The momentum transferred **to the wall** is $+2mv_x$.

Force exerted per collision on the wall

The time taken for the molecule to travel across the box and back to the same wall is:

$$\Delta t = \frac{2L}{v_x}$$

The rate of change of momentum (force f_x) exerted by one molecule is:

$$f_x = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L} \quad (2.21)$$

2.5.1 Pressure

The total force F_x exerted by all N molecules is:

$$F_x = \sum_{i=1}^N \frac{mv_{xi}^2}{L} = \frac{m}{L} \sum_{i=1}^N v_{xi}^2 \quad (2.22)$$

Pressure P is Force divided by Area ($A = L^2$):

$$P = \frac{F_x}{L^2} = \frac{m}{L^3} \sum v_{xi}^2 = \frac{m}{V} \sum v_{xi}^2 \quad (2.23)$$

Root Mean Square Velocity

Since the motion is random, the average velocity components are equal in all directions:

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle \quad (2.24)$$

Substituting $\sum v_{xi}^2 = N \langle v_x^2 \rangle = \frac{1}{3} N \langle v^2 \rangle$:

$$P = \frac{1}{3} \frac{Nm \langle v^2 \rangle}{V} \quad (2.25)$$

$$PV = \frac{1}{3}mN\langle v^2 \rangle \quad (2.26)$$

Defining the total mass $M = Nm$, density of the gas $\rho = M/V$ and $v_{rms} = \sqrt{\langle v^2 \rangle}$:

$$P = \frac{1}{3}\rho v_{rms}^2 \quad (2.27)$$

2.5.2 Kinetic Energy and Temperature

From the ideal gas law $PV = Nk_B T$ and 2.26:

$$\frac{1}{3}Nm v_{rms}^2 = Nk_B T \quad (2.28)$$

The average translational kinetic energy of a single molecule is:

$$\kappa_{avg} = \langle \frac{1}{2}mv^2 \rangle = \frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}mv_{rms}^2 = \frac{3}{2}k_B T \quad (2.29)$$

Insight

Temperature is a direct measure of the average translational kinetic energy of the molecules.

2.6 Principle of Equipartition of Energy

Statement of the Principle

For a dynamical system in thermal equilibrium at temperature T , the total energy is distributed equally among all its active degrees of freedom. The average energy associated with each individual degree of freedom is equal to $\frac{1}{2}k_B T$.

2.6.1 Consistency with Kinetic Theory

In our previous discussion on the kinetic theory of gases, we derived the equation of state for one mole of an ideal gas as $pV = RT$. From this, we established that the average translational kinetic energy of a molecule is:

$$\bar{\kappa} = \frac{3}{2}k_B T \quad (2.30)$$

Since a monoatomic gas is considered to have only translational motion in three-dimensional space ($f = 3$), this result is perfectly consistent with the Equipartition Principle, which assigns $\frac{1}{2}k_B T$ to each of the three translational axes (x, y, z).

2.6.2 Analysis of Degrees of Freedom (f)

- **Monoatomic Gas:** As confirmed by kinetic theory, these gases possess only translational degrees of freedom ($f = 3$).

$$u_{av} = 3 \times \left(\frac{1}{2} k_B T \right) = \frac{3}{2} k_B T \quad (2.31)$$

- **Diatomic Gas:** At standard temperatures, a diatomic molecule acts as a rigid rotator. It possesses 3 translational and 2 rotational degrees of freedom (rotation about the axis joining the two atoms is neglected as the moment of inertia is negligible), giving $f = 5$.

$$u_{av} = 5 \times \left(\frac{1}{2} k_B T \right) = \frac{5}{2} k_B T \quad (2.32)$$

unless Vibrational modes are activated.

- **Polyatomic Gas:** For more complex molecules, the situation includes:
 - **3 Translational modes.**
 - **3 Rotational modes** (or 2 if the molecule is linear).
 - **Vibrational modes:** Unlike translation or rotation, each vibrational mode contributes **two** degrees of freedom (one for kinetic energy and one for potential energy). Therefore, each active vibration contributes $1k_B T$ to the total energy.

💡 The "Frozen" Degrees of Freedom

It is important to note that vibrational modes (and sometimes rotational ones at very low temperatures) must be "activated" by reaching a specific temperature threshold. If the thermal energy is too low, these modes remain "frozen" and do not contribute to the heat capacity of the gas.

❓ Exercise

Given a non-linear triatomic molecule (like H_2O) where vibrations are neglected, calculate the total internal energy for 1 mole of the gas.

We will continue our discussion on various degree of freedom and associated energy with it in chapter 4

2.7 Maxwellian Distribution of an Ideal Gas

In a system of an ideal gas in thermal equilibrium at temperature T , the molecules move in random directions with varying speeds. The Maxwell-Boltzmann distribution describes the probability of a molecule having a specific velocity.

💡 The Maxwell-Boltzmann distribution

Maxwell and Boltzmann figured out that any function of energy for an individual molecule in thermal equilibrium can be described by a specific distribution.

Discrete Form: The number of molecules n_i in a state with energy ϵ_i is proportional to the Boltzmann factor:

$$n_i \propto e^{-\frac{\epsilon_i}{k_B T}} \quad (2.33)$$

$$n_i = \frac{N}{Z} e^{-\frac{\epsilon_i}{k_B T}} \quad (2.34)$$

where $N = \sum n_i$ and $Z = \sum e^{-\epsilon_i/k_B T}$ is the partition function.

Continuous Form: For a continuous range of energies, the probability density (making sure $\int f(\epsilon) d\epsilon = 1$) is:

$$\frac{N_\epsilon d\epsilon}{N} = f(\epsilon) d\epsilon = A e^{-\frac{\epsilon}{k_B T}} d\epsilon \quad (2.35)$$

where A is a normalization constant.

$N_\epsilon d\epsilon$ is number of molecules in the range of ϵ to $\epsilon + d\epsilon$ interval.

$\frac{N_\epsilon d\epsilon}{N} = f(\epsilon) d\epsilon$ is the probability of finding that molecule (we chosen randomly) at the energy ϵ to $\epsilon + d\epsilon$ interval.

Based on the Boltzmann factor $e^{-\epsilon/k_B T}$, where $\epsilon = \frac{1}{2}mv^2$.

Out of total N molecules, Number of molecules in the velocity range from v_x to $v_x + dv_x$ will be:

$$N_{v_x} dv_x = A' \exp\left(-\frac{mv_x^2}{2k_B T}\right) dv_x \quad (2.36)$$

Hence the probability of finding a molecule in in the velocity range from v_x to $v_x + dv_x$ will be $\frac{N_{v_x} dv_x}{N} = f(v_x) dv_x$:

$$f(v_x) dv_x = A \exp\left(-\frac{mv_x^2}{2k_B T}\right) dv_x \quad (2.37)$$

where $A = \frac{A'}{N}$.

Normalization Constant

Since $f(v_x)$ is a probability density, it must satisfy the normalization condition

$$\int_{-\infty}^{\infty} f(v_x) dv_x = 1. \quad (2.38)$$

Substituting the expression for $f(v_x)$,

$$A \int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2k_B T}} dv_x = 1. \quad (2.39)$$

Using the standard Gaussian integral

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}, \quad (2.40)$$

we obtain

$$\int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2kT}} dv_x = \sqrt{\frac{2\pi kT}{m}}. \quad (2.41)$$

which yields

$$A = \sqrt{\frac{m}{2\pi kT}}. \quad (2.42)$$

2.7.1 Velocity distribution

Substituting the value of A , the Maxwell distribution for one velocity component becomes

$$f(v_x)dv_x = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{mv_x^2}{2k_B T}\right) dv_x \quad (2.43)$$

If We ask, what will be probability of randomly choosing molecule to have velocity in the (infinitesimal volume $d^3\vec{v}$) range of $\vec{v} = (v_x, v_y, v_z)$ to $\vec{v} + d^3\vec{v} = (v_x + dv_x, v_y + dv_y, v_z + dv_z)$.

Because the gas is isotropic, the motions in the x, y , and z directions are independent, meaning:

$$f(\vec{v})d^3\vec{v} = f(v_x)f(v_y)f(v_z)dv_xdv_ydv_z \quad (2.44)$$

Multiplying the three independent components together, we get the velocity vector distribution:

$$f(v_x, v_y, v_z)d^3v = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T}\right) dv_xdv_ydv_z \quad (2.45)$$

Since the energy of a molecule is purely kinetic, $\epsilon = \frac{1}{2}mv^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$, the probability of finding a molecule with a specific velocity vector is:

$$f(\vec{v})d^3\vec{v} = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right) d^3\vec{v} \quad (2.46)$$

Here volume element d^3v See Appendix

$$d^3\vec{v} = dv_xdv_ydv_z = v^2 \sin\theta d\theta d\phi \quad (\text{Spherical coordinates}) \quad (2.47)$$

Probability of finding a molecule at speed v :

$$F(v)dv = \left(\int_{\theta=0}^{\pi} \sin\theta d\theta \int_{\phi=0}^{2\pi} d\phi\right) v^2 f(v)dv \quad (2.48)$$

$$F(v)dv = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) dv \quad (2.49)$$

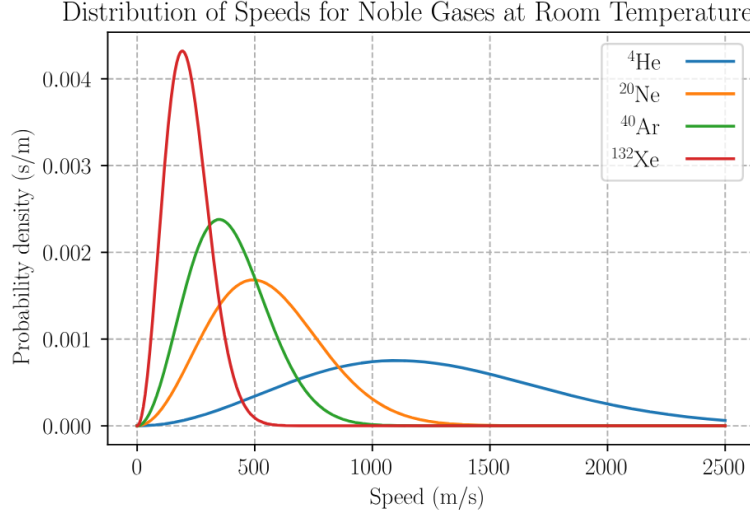


Figure 2.2: Velocity distributions of inert gases

Most Probable Speed (v_{mp})

This is found by setting $\frac{dF(v)}{dv} = 0$:

$$\frac{d}{dv} \left[v^2 \exp \left(-\frac{mv^2}{2k_B T} \right) \right] = 0 \quad (2.50)$$

yields:

$$v_{mp} = \sqrt{\frac{2k_B T}{m}} \quad (2.51)$$

Average Speed (v_{avg})

The average is the first moment of the distribution:

$$\langle v \rangle = \int_0^\infty v F(v) dv = \sqrt{\frac{8k_B T}{\pi m}} \quad (2.52)$$

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}} \quad (2.53)$$

Root Mean Square Speed (v_{rms})

The mean square speed is the second moment:

$$\langle v^2 \rangle = \int_0^\infty v^2 F(v) dv = \frac{3k_B T}{m} \quad (2.54)$$

$$v_{rms} = \sqrt{\frac{3k_B T}{m}} \quad (2.55)$$

The relationship between these speeds is:

$$v_{mp} < v_{avg} < v_{rms} \quad (2.56)$$

2.7.2 Momentum

Using $p = mv$, the distribution of momentum magnitude is:

$$F(p)dp = 4\pi \left(\frac{1}{2\pi m k_B T} \right)^{3/2} p^2 \exp \left(-\frac{p^2}{2m k_B T} \right) dp \quad (2.57)$$

2.7.3 Energy Distribution

The kinetic energy of a gas molecule is given by

$$\epsilon = \frac{1}{2}mv^2. \quad (2.58)$$

Using the Maxwell velocity distribution and transforming from velocity space to energy space, the distribution of translational energy is obtained as

$$F(\epsilon) d\epsilon = \frac{2}{\sqrt{\pi}} \frac{1}{(kT)^{3/2}} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon. \quad (2.59)$$

Average energy

This distribution shows that molecular energies are not equal but are spread over a range of values, with the mean energy given by

$$\langle \epsilon \rangle = \frac{3}{2}kT. \quad (2.60)$$

Using $\epsilon = \frac{1}{2}mv^2$, we transform the variable to energy:

$$F(\epsilon)d\epsilon = \frac{2\sqrt{\epsilon}}{\sqrt{\pi}(k_B T)^{3/2}} \exp \left(-\frac{\epsilon}{k_B T} \right) d\epsilon \quad (2.61)$$

2.8 Transport phenomenon

2.8.1 Mean free path

The *mean free path* (λ) is defined as the average distance traveled by a gas molecule between two successive collisions.

Collision Rate

Consider a single molecule (as hard spheres of diameter d), moving with speed v through a background of identical molecules with number density n (molecules per unit volume). A collision occurs whenever the centers of two molecules come within a distance d of each other.

During a short time interval dt , the molecule sweeps out a cylindrical volume:

$$dV = \sigma v dt = \pi d^2 v dt \quad (2.62)$$

where $\sigma = \pi d^2$ is the effective collision cross-section. The number of molecules dN within this volume (and thus the number of collisions) is:

$$dN = n(\pi d^2 v dt) \quad (2.63)$$

The collision frequency f is the number of collisions per unit time:

$$f = \frac{dN}{dt} = n\pi d^2 v \quad (2.64)$$

Mean Free Path

The average time between collisions, known as the *mean free time* (τ), is the reciprocal of the frequency:

$$\tau = \frac{1}{n\pi d^2 v} \quad (2.65)$$

The mean free path λ is the distance covered during this time:

$$\lambda = v\tau = \frac{1}{n\pi d^2} \quad (2.66)$$

Correction for Relative Motion (First Order Approximation)

The initial derivation assumes "target" molecules are stationary. In reality, all molecules are moving randomly. To account for this, we must use the average relative velocity v_{rel} .

For any two molecules with velocities \vec{v}_1 and \vec{v}_2 , the relative velocity is $\vec{v}_{rel} = \vec{v}_1 - \vec{v}_2$. Squaring this gives:

$$v_{rel}^2 = v_1^2 + v_2^2 - 2\vec{v}_1 \cdot \vec{v}_2 \quad (2.67)$$

Taking the average over the distribution:

1. Due to random motion, the dot product term $2\vec{v}_1 \cdot \vec{v}_2$ averages to zero.

2. Since the molecules are identical, $\langle v_1^2 \rangle = \langle v_2^2 \rangle = \langle v^2 \rangle$.

Thus, $\langle v_{rel}^2 \rangle = 2\langle v^2 \rangle$, which implies $v_{rel} = \sqrt{2}v$. Substituting this into our collision frequency calculation yields the corrected mean free path:

$$\lambda = \frac{1}{\sqrt{2}n\pi d^2} \quad (2.68)$$

Dependence on Temperature and Pressure

Using the ideal gas law $P = nk_B T$, we substitute $n = \frac{P}{k_B T}$:

$$\lambda = \frac{k_B T}{\sqrt{2}\pi d^2 P} \quad (2.69)$$

- Typical values of the mean free path in gases at atmospheric pressure are of the order of 10^{-7} m.



Survival Equation

Number of particles surviving collisions in traveling a distance x :

$$N(x) = N(0) \exp\left(-\frac{x}{\lambda}\right) \quad (2.70)$$



Microscopic motion to Macroscopic transport

The mean free path provides the crucial link between the microscopic motion of molecules and the macroscopic transport properties of gases.

Transport Phenomena in Gases

When a gas is not in equilibrium—due to differences in temperature, velocity, or concentration—random molecular motion acts to equalize these gradients. This process is known as *transport phenomena*. Molecules "transport" physical quantities as they move through their mean free path (λ).

Table 2.1: Primary Transport Phenomena

Phenomenon	Quantity Transported	Driving Gradient	Coefficient
Viscosity	Momentum (mv)	Velocity (du/dz)	Viscosity (η)
Thermal Conduction	Heat Energy	Temperature (dT/dz)	Conductivity (K)
Diffusion	Mass/Molecules	Concentration (dn/dz)	Diffusion (D)

2.8.2 Viscosity: The Transport of Momentum

Viscosity is the internal friction of a gas, resulting from the transfer of momentum from high-velocity layers to low-velocity layers.

Consider a gas flowing in the x -direction with a velocity gradient du/dz along the z -axis. Consider an imaginary plane P at height z where the flow velocity is u .

- Molecules reaching P from **above** ($z + \lambda$) carry momentum: $m(u + \lambda \frac{du}{dz})$.
- Molecules reaching P from **below** ($z - \lambda$) carry momentum: $m(u - \lambda \frac{du}{dz})$.

Let n be the number density and \bar{v} be the average thermal speed. Statistically, the number of molecules crossing the plane P per unit area per unit time from one side (assuming movement in six directions) is $\frac{1}{6}n\bar{v}$.

The downward momentum flux p_{\downarrow} is:

$$p_{\downarrow} = \frac{1}{6}nm\bar{v} \left(u + \lambda \frac{du}{dz} \right) \quad (2.71)$$

The upward momentum flux p_{\uparrow} is:

$$p_{\uparrow} = \frac{1}{6}nm\bar{v} \left(u - \lambda \frac{du}{dz} \right) \quad (2.72)$$

The net momentum transfer per unit area per unit time (shear stress or viscous force τ) is the difference:

$$\tau = p_{\downarrow} - p_{\uparrow} = \frac{1}{6}nm\bar{v} \left(2\lambda \frac{du}{dz} \right) = \frac{1}{3}nm\bar{v}\lambda \frac{du}{dz} \quad (2.73)$$

By Newton's Law of Viscosity, $\tau = \eta \frac{du}{dz}$. Comparing the expressions, we find:

$$\boxed{\eta = \frac{1}{3}nm\bar{v}\lambda} \quad (2.74)$$

Properties of Gas Viscosity

1. **Pressure Independence:** Since $\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$, substituting this into η cancels n . Thus, η is independent of pressure for an ideal gas.
2. **Temperature Dependence:** Since $\bar{v} \propto \sqrt{T}$, the viscosity increases with temperature: $\eta \propto \sqrt{T}$.

2.8.3 Thermal Conduction: Transport of Energy

Thermal conduction is the process by which kinetic energy is transported from a high-temperature region to a low-temperature region.

Let ϵ be the average kinetic energy of a molecule. In a temperature gradient dT/dz , the energy of a molecule is $\epsilon = C_v T$, where c_v is the molecular heat capacity.

The energy carried by molecules crossing a plane z from the hotter side ($z + \lambda$) and colder side ($z - \lambda$) results in a net heat flux q :

$$q = \frac{1}{6}n\bar{v} \left(\epsilon - \lambda \frac{d\epsilon}{dz} \right) - \frac{1}{6}n\bar{v} \left(\epsilon + \lambda \frac{d\epsilon}{dz} \right) \quad (2.75)$$

$$q = -\frac{1}{3}n\bar{v}\lambda \frac{d\epsilon}{dz} \quad (2.76)$$

Since $\frac{d\epsilon}{dz} = \frac{d\epsilon}{dT} \frac{dT}{dz} = C_v \frac{dT}{dz}$:

$$q = -\left(\frac{1}{3}n\bar{v}\lambda C_v \right) \frac{dT}{dz} \quad (2.77)$$

Comparing this to Fourier's law $q = -K \frac{dT}{dz}$, we find the thermal conductivity:

$$\boxed{K = \frac{1}{3}n\bar{v}\lambda C_v} \quad (2.78)$$

properties of Thermal conductivity

- **Pressure Independence:** In both η and K , the term $n\lambda$ appears. Since $\lambda \propto 1/n$, the density cancels out, making both coefficients independent of pressure.
- **Relationship:**

$$\frac{K}{\eta} = \frac{C_v}{m} = s_v \quad (2.79)$$

$$\boxed{K = \eta m C_v} \quad (2.80)$$

It shows that, gases with high viscosity are typically also good thermal conductors.

2.8.4 Self-Diffusion: Transport of Mass

Self-diffusion refers to the transport of molecules within a gas due to a concentration gradient dn/dz .

Let n be the number density of a specific type of molecule (or labeled molecules). The number of molecules crossing a plane P per unit area per unit time is $\frac{1}{6}\bar{v}n$.

In the presence of a gradient, the net flux J is the difference between those moving up from a region of density $(n - \lambda \frac{dn}{dz})$ and those moving down from $(n + \lambda \frac{dn}{dz})$:

$$J = \frac{1}{6}\bar{v} \left(n - \lambda \frac{dn}{dz} \right) - \frac{1}{6}\bar{v} \left(n + \lambda \frac{dn}{dz} \right) \quad (2.81)$$

$$J = -\frac{1}{3}\bar{v}\lambda \frac{dn}{dz} \quad (2.82)$$

Comparing this to Fick's Law, $J = -D \frac{dn}{dz}$, we find the diffusion coefficient:

$$\boxed{D = \frac{1}{3}\bar{v}\lambda} \quad (2.83)$$

This relationship implies that as a gas becomes less dense, its molecules diffuse more rapidly.



Einstein and the Diffusion Coefficient

In 1905, **Albert Einstein** provided the first quantitative explanation of diffusion through his theory of *Brownian motion*. He showed that the diffusion coefficient is not merely a phenomenological constant but is fundamentally connected to thermal agitation and molecular mobility.

For a particle undergoing random thermal motion in a fluid, Einstein derived the relation

$$D = \mu k_B T, \quad (2.84)$$

where μ is the mobility of the particle, k_B is Boltzmann's constant, and T is the absolute temperature.

This result, known as the **Einstein diffusion relation**, bridges microscopic dynamics and macroscopic transport laws. In gases, the kinetic-theory expression

$$D = \frac{1}{3}\bar{v}\lambda$$

emerges naturally as a specific realization of Einstein's general framework, with the mean free path λ and average molecular speed \bar{v} encoding molecular mobility.

Einstein's work not only confirmed the atomic nature of matter but also established diffusion as a cornerstone of modern statistical mechanics.

Chapter 3

Real Gases

3.1 Andrews' Experiment on CO_2

In an attempt to liquefy CO_2 at different temperatures, Thomas Andrews conducted experiments in 1869. He applied pressure while keeping Temperature fixed, and observe how volume changes with pressure.

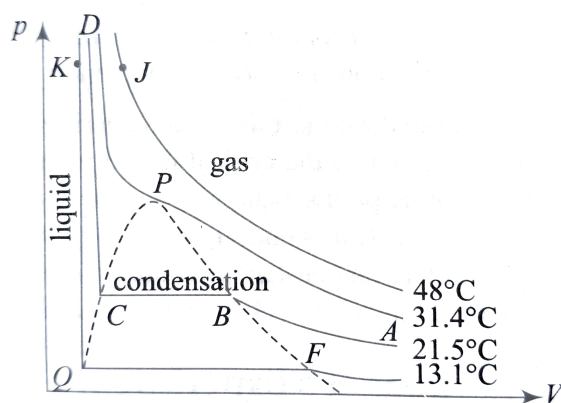


Figure 3.1: Andrew's Isotherms of CO_2

key observations:

- At high temperatures, the isotherms resemble those predicted by the ideal gas law ($PV = \text{Constant}$, Rectangular Hyperbola).
- At lower temperatures, the isotherms exhibit a horizontal portion CB, where pressure remains constant over a range of volumes. (sudden shrink in gas volume, Condensation of gas into liquid), This horizontal region CB corresponds to the coexistence of liquid and gaseous phases.
- As the temperature increases, the horizontal portion of the isotherm shortens and finally disappears at a particular temperature (Point P) called the **critical temperature** $T_c = 31.4^\circ C$.

At the critical point P:

The pressure and volume at this point are known as the **critical pressure** P_c and **critical volume** V_c , respectively.

- **Critical Temperature** (T_c): The temperature above which a gas cannot be liquefied by pressure alone.
- **Critical Pressure** (p_c): The pressure required for liquefaction at T_c .
- **Critical Volume** (V_c): The volume occupied by 1 mole at p_c and T_c .

- At 13.4°C, CO_2 begins to liquefy at approximately 50 atm (Point P). During liquefaction, pressure remains constant (Line BC) until the gas is entirely liquid. The steep curve CD and QK shows that liquids are highly incompressible.
- The critical point (T_c, P_c, V_c) is a point of inflection (where curve goes concave to convex).

The critical point corresponds to a point of inflection on the critical isotherm:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0, \quad (3.1)$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0. \quad (3.2)$$

3.2 Van der Waals Gas Equation

The ideal gas equation of state assumes that gas molecules occupy negligible volume and exert no forces on one another.

In real gases, both assumptions fail. van der Waals introduced corrections to account for the finite size of molecules and intermolecular attractions.

3.2.1 Correction for Finite Molecular Volume

Real gas molecules have a finite size and therefore exclude a certain volume from being available for molecular motion. Lets calculate the volume not available to a molecule in Total Volume V ,

When two hard spherical molecules of radius r approach each other, the center of one molecule cannot come within a distance $2r$ of the center of the other. Hence, the unavailable volume around each molecule is a sphere of radius $2r$.

The non-available volume at per two molecule location is therefore

$$v'_{\text{non-available}} = \frac{4}{3}\pi(2r)^3 = 8\left(\frac{4}{3}\pi r^3\right). \quad (3.3)$$

Since this non-available volume is shared equally between two molecules, the effective non-available volume per molecule becomes

$$v_{\text{non-available}} = \frac{v'_{\text{non-available}}}{2} = 4 \left(\frac{4}{3} \pi r^3 \right). \quad (3.4)$$

If there are n mole (gas of N molecules, $N = nN_A$) of molecule are in total Volume V , than non-available Volume to a molecule will be

$$V_{\text{non-available}} = 4nN_A \left(\frac{4}{3} \pi r^3 \right) \quad (3.5)$$

In the ideal gas scene, gas in volume V (number of moles = n) has a volume of V available for molecular motion. Here, the volume available for molecular motion will be reduced by $V_{\text{non-available}}$. where

$$V_{\text{available}} = V - V_{\text{non-available}}. \quad (3.6)$$

Accordingly, the volume V in the ideal gas equation must be replaced by $V - 4nN_A \left(\frac{4}{3} \pi r^3 \right)$. Ideal gas equation now reduced to

$$PV_{\text{available}} = nRT \quad (3.7)$$

$$P \left[V - 4nN_A \left(\frac{4}{3} \pi r^3 \right) \right] = nRT \quad (3.8)$$

or we can introduce a parameter b such that

$$P(V - nb) = nRT \quad (3.9)$$

where b is the volume not available for a molecule for motion in Volume V , that contains 1 mole of gas.

$$\boxed{b = 4N_A \left(\frac{4}{3} \pi r^3 \right) = \frac{1}{n} V_{\text{non-available}}} \quad (3.10)$$

3.2.2 Correction for Intermolecular Attraction

In a real gas, attractive forces act between molecules. A molecule approaching the container wall experiences an inward pull due to neighboring molecules, resulting in a reduction of momentum transferred to the wall. Consequently, the observed pressure P is less than the pressure P_{ideal} that would be exerted in the absence of intermolecular attractions.

The magnitude of this pressure reduction depends on the number of interacting molecular pairs density. In Gas of N molecules, one molecule can make pair with $(N - 1)$ other molecules. hence total of N molecules can make $N(N - 1)/2 \propto N^2$ pairs.

number of interacting pairs per unit volume

$$\text{pair density} \propto \frac{N^2}{V^2} \quad (3.11)$$

Since pressure is determined by local molecular interactions near the container wall and intermolecular attraction is a pairwise effect, the reduction in pressure is proportional to the local density of interacting molecular pairs, which varies as the square of molecular density

$$\Delta P \propto \frac{N^2}{V^2} \quad (3.12)$$

$$P_{ideal} - P = \frac{an^2}{V^2} \quad (3.13)$$

where a is a constant characteristic of the strength of intermolecular attraction. P_{ideal} is given by Eq. 3.9

$$P_{ideal} = \frac{nRT}{(V - nb)} \quad (3.14)$$

By equation 3.13 and 3.14 :

$$\left(P + \frac{n^2a}{V^2} \right) (V - nb) = nRT. \quad (3.15)$$

- The constant a measures the strength of intermolecular attraction. and Hence Larger values of a correspond to gases that are more easily liquefied.
- The constant b represents the effective molecular volume.

Johannes Diderik van der Waals

His equation of state was the first to bridge the gap between gases and liquids, establishing the principle of the "continuity of states".

Limitations of van der Waals Equation

Despite its success, the van der Waals equation has limitations:

- It fails to accurately predict behavior near the critical point.
- Quantitative agreement with experiments is limited.
- It does not account for molecular shape or quantum effects.

Nevertheless, it represents a major improvement over the ideal gas model.

3.3 Characteristic Temperatures of a vdW gas

Critical Temperature

The *critical temperature* T_c of a gas is the highest temperature above which the gas cannot be liquefied by the application of pressure alone.

For a van der Waals gas, the critical temperature is obtained from the critical point conditions

$$\left(\frac{\partial P}{\partial V} \right)_T = 0, \quad \left(\frac{\partial^2 P}{\partial V^2} \right)_T = 0,$$

and is given by

$$T_c = \frac{8a}{27Rb}.$$

Boyle Temperature

The *Boyle temperature* T_B is the temperature at which a real gas obeys Boyle's law most closely over an extended range of pressures.

At this temperature, the second virial coefficient vanishes:

$$B(T_B) = 0.$$

For a van der Waals gas,

$$B(T) = b - \frac{a}{RT},$$

which gives

$$T_B = \frac{a}{Rb}.$$

Temperature of Inversion

The *temperature of inversion* T_i is the temperature at which the Joule–Thomson coefficient

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H$$

changes sign.

For a van der Waals gas, the Joule–Thomson coefficient is

$$\mu_{JT} = \frac{1}{C_P} \left(\frac{2a}{RT} - b \right).$$

Setting $\mu_{JT} = 0$, the (maximum) inversion temperature is

$$T_i = \frac{2a}{Rb}.$$

Relationship Between the Temperatures

Using the above expressions, we obtain

$$T_i = 2T_B, \quad T_c = \frac{8}{27}T_B,$$

and hence

$$T_i = \frac{27}{4}T_c.$$

? Important Exercise

- (a) Determine the SI units for the van der Waals constants a and b based on the equation 3.15.
- (b) Calculate Critical constants using Eq. 3.1 and 3.2 for Van der waals Equation of state.

Answer:

$$V_c = 3b, \quad (3.16)$$

$$P_c = \frac{a}{27b^2}, \quad (3.17)$$

$$T_c = \frac{8a}{27Rb}. \quad (3.18)$$

- (c) Determine the work performed by a gas following a van der Waals equation during isothermal expansion.
- (d) Using Molar Volume $V_m = \frac{V}{n}$, Find the Value of Compressibility factor $Z = \frac{PV_m}{RT}$ for the vdW Equation of state and expand in terms of Negative power of V_m .
- (e) Solve $\left. \frac{\delta Z}{\delta \rho} \right|_{\rho=0, T=T_B} = 0$ where $\rho = V_m^{-1}$: molar density for vdW equation of state. where T_B is known as Boyle Temperature.

answer:

$$T_B = \frac{a}{Rb} \quad (3.19)$$

- (f) for dilute gas ($\rho \xrightarrow[\text{dilute gas}]{\text{high } V_m} 0$), proof that vdW Equation of state reduces to:

$$PV = nRT_B \quad (3.20)$$

- (g) Determine the temperature (T_i called inversion Temperature) at which the condition

$$T \left(\frac{\partial V}{\partial T} \right)_P = V$$

is satisfied.

answer:

$$T_i = \frac{2a}{Rb} \quad (3.21)$$

- (h) difference of heat capacities is given by:

$$\boxed{C_P = C_V + P \left(\frac{\partial V}{\partial T} \right)_P} \quad (3.22)$$

calculate $C_P - C_V$ for van-der waals gas.

- (i) Try all the above calculations for other Equation of states given in the Appendix B

3.4 Virial Equation of State



Kamerling Onnes

The same guy famous for discovering superconductivity, Also studied the behaviour of real gases. He proposed an idea of write real gas equation as virial equation.

A more general description of real gases is provided by the virial equation of state:

$$Z = \frac{PV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \dots \quad (3.23)$$

where $B(T)$, $C(T)$, etc., are temperature-dependent virial coefficients. These coefficient represents contributions from two-body, three-body and higher-order intermolecular interactions.

since, Molar density $\rho = \frac{n}{V} = V_m^{-1}$,

Equation 3.23 takes the following form:

$$Z = \frac{P}{\rho RT} = 1 + B(T)\rho + C(T)\rho^2 + \dots \quad (3.24)$$

- The second coefficient B is particularly important; it represents pairwise molecular interactions.
- The **Boyle Temperature** is defined as the temperature at which $B = 0$, where the gas obeys Boyle's law over a wide range of pressure.
- factor $Z = \frac{PV}{nRT} = \frac{PV_m}{RT} = \frac{P}{\rho RT}$ is called **compressibility factor**. For Ideal gas, $Z = 1$. And for real gases it deviates from 1.

Chapter 4

First Law of Thermodynamics

4.1 Point Function and Path Function

In thermodynamics, physical quantities are classified according to whether their values depend only on the state of the system or also on the manner in which the process is carried out. This leads to the concepts of *point functions* and *path functions*.

Point Function (State Function)

A **point function**, also called a *state function*, is a quantity whose value depends only on the state of the system and not on the path followed to reach that state.

If a system changes from an initial state A to a final state B , the change in a point function is uniquely determined by these two states:

$$\Delta X = X(B) - X(A), \quad (4.1)$$

and is independent of the intermediate steps of the process.

Mathematically, the differential of a point function is an *exact differential*, denoted by dX .

Examples of point functions:

Internal energy (U), Entropy (S), Enthalpy (H), Pressure (P), Volume (V), Temperature (T)

For a cyclic process,

$$\oint dX = 0, \quad (4.2)$$

which is a defining property of point functions.

Path Function

A **path function** is a quantity whose value depends on the path taken during a process and not solely on the initial and final states.

For a process from state A to state B , the value of a path function differs for different paths connecting the same states.

The differential of a path function is an *inexact differential* and is represented by symbols such as δQ or δW .

Examples of path functions:

- Heat (Q)

- Work (W)

For a cyclic process,

$$\oint \delta Q \neq 0, \quad \oint \delta W \neq 0, \quad (4.3)$$

in general.

💡 System possess State functions of it

Point functions represent properties stored in the system and characterize its equilibrium state. Path functions, on the other hand, represent modes of energy transfer across the system boundary during a process.

Thus, a system *possesses* internal energy or entropy, but it does not *possess* heat or work.

4.2 Internal Energy: The 1st Thermodynamic Potential

Internal energy is the total energy contained within a thermodynamic system. It is a State Function, meaning its value is determined solely by the current state of the system and not by how the system reached that state.

From a microscopic perspective, a system (such as a gas) consists of molecules in constant, random motion. The total energy of these molecules can be broken down into several components based on their Degrees of Freedom:

Translational Kinetic Energy (K_{trans}): Energy due to the linear motion of the center of mass of molecules. For the i^{th} molecule:

$$K_{trans,i} = \frac{1}{2}mv_i^2$$

Rotational Kinetic Energy (K_{rot}): Energy associated with the rotation of molecules about their axes:

$$K_{rot,i} = \frac{1}{2}I\omega_i^2$$

Vibrational Energy (E_{vib}): Energy from the internal oscillation of atoms within a molecule (possessing both kinetic and potential components):

$$E_{vib,i} = K_{vib} + U_{vib}$$

Intermolecular Potential Energy (U_{pot}): Energy due to the forces of attraction (Van der Waals forces) or repulsion between molecules.

The **Internal Energy (U)** is the sum of all these microscopic forms of energy for all N particles in the system:

$$U = \sum_{i=1}^N \left(\frac{1}{2}mv_i^2 + \frac{1}{2}I\omega_i^2 + E_{vib,i} \right) + U_{potential} + \dots \quad (4.4)$$

For an **Ideal Gas**, we assume that intermolecular forces are negligible ($U_{potential} \approx 0$). Thus, the internal energy of an ideal gas is purely a sum of the kinetic energies of its molecules.

4.2.1 Joule Expansion

In this experiment, a gas expands into a vacuum within a thermally insulated container. During the expansion, the Volume (V) increases and the Pressure (P) decreases. Despite the massive changes in P and V , the **Temperature** (T) of the gas remains constant (isothermal process).

Argument

Since the state changed (P and V altered) but the internal energy remained constant (as no work was done and no heat was exchanged), Joule concluded that U does not depend on volume or pressure. Instead, it is linked to the variable that did not change: Temperature.

Conclusion

For an ideal gas, the internal energy is a function of **absolute temperature only**:

$$U = U(T) \quad (4.5)$$

This implies that as long as the temperature of an ideal gas is constant, its internal energy remains unchanged, regardless of how the pressure or volume varies.

4.3 The First Law of Thermodynamics

The First Law of Thermodynamics is a statement of the conservation of energy.

The heat δQ supplied to a system is used partly to increase the internal energy of the system and partly to perform work.

In finite form, the First Law is written as

$$Q = \Delta U + W \quad (4.6)$$

where W is the work done by the system.

In differential form,

$$\delta Q = dU + \delta W \quad (4.7)$$

or, equivalently, the more convenient form,

$$dU = \delta Q - \delta W \quad (4.8)$$

4.3.1 Mechanical (pressure–volume) work

If a gas exerts pressure P on its surroundings and its volume changes from V to $V + dV$, the infinitesimal work done by the system is

$$\delta W = P dV \quad (4.9)$$

Hence, the First Law becomes

$$dU = \delta Q - P dV \quad (4.10)$$

4.3.2 Generalized work

In a general system, work may be performed by forces other than pressure. Suppose generalized forces J_i act on the system and produce corresponding infinitesimal generalized displacements dX_i . Then the generalized work done *on* the system is

$$\delta W' = \sum_i J_i dX_i \quad (4.11)$$

Here, J_i are called generalized forces and X_i are the corresponding generalized displacements.

System	Generalized Force	Generalized Displacement	Work Term
Stretched wire	Tension F	Length dL	$F dL$
Liquid film	Surface tension γ	Area dA	γdA
Magnetic material	Magnetic field H	Magnetization dM	$H dM$
Dielectric	Electric field E	Polarization dP	$E dP$

Table 4.1: Examples of generalized work terms

The First Law including generalized work terms may be written as

$$\delta Q + \delta W' = dU + \delta W \quad (4.12)$$

where the left-hand side represents energy supplied to the system (heat and work done on the system), while the right-hand side represents the increase in internal energy and the work done by the system.

Thus, the First Law takes the generalized form

$$dU = \delta Q - P dV + \sum_i J_i dX_i \quad (4.13)$$

We can include the term $-P dV$ in $J_k dX_k$ by identifying the pressure as a generalised force and the volume as the corresponding generalised displacement. Thus, taking

$$J_k = -P, \quad X_k = V,$$

the work term is written as

$$\delta W = J_k dX_k = -P dV.$$

$$\boxed{dU = \delta Q + \sum_i J_i dX_i} \quad (4.14)$$

4.3.3 Chemical work and chemical potential

In systems where the number of particles is not conserved (such as open systems, chemical reactions, or particle exchange with a reservoir), an additional form of work appears known as *chemical work*.

If N_i denotes the number of particles of the i -th species and μ_i is the corresponding chemical potential, then the chemical work term is

$$\delta W_{\text{chem}} = - \sum_i \mu_i dN_i \quad (4.15)$$

The negative sign indicates that an increase in particle number increases the internal energy of the system.

Including chemical work, the most general form of the First Law becomes

$$\boxed{dU = \delta Q + \sum_i J_i dX_i + \sum_i \mu_i dN_i} \quad (4.16)$$

4.4 Applications of the First Law of Thermodynamics

4.4.1 Heat Capacity (C)

The heat capacity of a system is defined as the amount of heat required to raise the temperature of a substance containing n moles by one degree (1 K or 1°C). It is defined as

$$C = \frac{\delta Q}{dT} \quad \Longrightarrow \quad \delta Q = C dT \quad (4.17)$$

Since gases are compressible, the heat required to produce a given temperature change depends on the conditions under which heating takes place. Therefore, different heat capacities are defined depending on whether the volume or the pressure of the system is kept constant.

Heat Capacity at Constant Volume (C_V)

Consider a gas confined in a rigid container so that the volume remains constant ($dV = 0$). The work done by the system is then

$$\delta W = P dV = 0 \quad (4.18)$$

According to the First Law of Thermodynamics,

$$dU = \delta Q_V \quad (4.19)$$

Hence, the heat supplied at constant volume goes entirely into increasing the internal energy of the system. The heat capacity at constant volume is therefore defined by

$$\boxed{dU = C_V dT} \quad (4.20)$$

For an ideal gas, the internal energy U is a function of temperature only. Consequently, the relation $dU = C_V dT$ holds for an ideal gas irrespective of the nature of the process.

Heat Capacity at Constant Pressure (C_P)

If a gas is heated while maintaining constant pressure, the system is allowed to expand. In this case, the heat supplied to the system is partly used to increase the internal energy and partly to perform expansion work.

From the First Law,

$$\delta Q_P = dU + P dV \quad (4.21)$$

By definition,

$$\delta Q_P = C_P dT \quad (4.22)$$

Therefore,

$$C_P = \left(\frac{\delta Q}{dT} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \quad (4.23)$$

Using the definition of C_V , this may be written as

$$\boxed{C_P = C_V + P \left(\frac{\partial V}{\partial T} \right)_P} \quad (4.24)$$

Since the system performs work during expansion at constant pressure, a greater amount of heat is required to produce the same temperature rise than in the constant volume case. Hence,

$$C_P > C_V \quad (4.25)$$

💡 Mayer's relation

For an ideal gas obeying the equation of state $PV = nRT$,

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{nR}{P} \quad (4.26)$$

Substituting into the previous equation, we obtain Mayer's relation.

$$\boxed{C_P - C_V = nR} \quad (4.27)$$

4.4.2 Adiabatic Process: Derivation of $PV^\gamma = \text{constant}$

For an adiabatic process, no heat is exchanged with the surroundings:

$$\delta Q = 0 \quad (4.28)$$

The First Law of Thermodynamics,

$$dU = \delta Q - P dV, \quad (4.29)$$

therefore reduces to

$$dU = -P dV. \quad (4.30)$$

For an ideal gas, the internal energy depends only on temperature:

$$dU = C_V dT. \quad (4.31)$$

Hence,

$$C_V dT = -P dV. \quad (4.32)$$

The equation of state of an ideal gas is

$$PV = nRT, \quad (4.33)$$

which implies

$$P dV + V dP = nR dT. \quad (4.34)$$

Using the definition of heat capacities:

At constant pressure,

$$\delta Q_P = C_P dT = dU + P dV, \quad (4.35)$$

which gives

$$C_P = C_V + P \left(\frac{\partial V}{\partial T} \right)_P. \quad (4.36)$$

For an ideal gas,

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{nR}{P}, \quad (4.37)$$

and therefore Mayer's relation follows:

$$C_P - C_V = nR. \quad (4.38)$$

Combining Eqs. (4.32) and (4.34):

Eliminating dT between the two equations and using $\gamma = C_P/C_V$, we obtain

$$\frac{dP}{P} + \gamma \frac{dV}{V} = 0. \quad (4.39)$$

Integrating,

$$\boxed{PV^\gamma = \text{constant}}. \quad (4.40)$$

Example: Adiabatic Condition for a Van der Waals Gas

For a Van der Waals gas, the equation of state is

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT, \quad (4.41)$$

where a and b are the Van der Waals constants accounting for intermolecular attraction and finite molecular volume respectively.

First Law of Thermodynamics

For an adiabatic process,

$$\delta Q = 0, \quad (4.42)$$

and hence, from the first law of thermodynamics,

$$dU = \delta W. \quad (4.43)$$

For a reversible process, the work done is

$$\delta W = -P dV. \quad (4.44)$$

Internal Energy of a Van der Waals Gas

The differential form of internal energy for a real gas is

$$dU = C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV. \quad (4.45)$$

For a Van der Waals gas,

$$\left(\frac{\partial U}{\partial V} \right)_T = \frac{a}{V^2}, \quad (4.46)$$

which represents the contribution of intermolecular forces.

Thus,

$$dU = C_V dT + \frac{a}{V^2} dV. \quad (4.47)$$

Adiabatic Condition

Using $dU = -P dV$, we obtain

$$C_V dT + \frac{a}{V^2} dV + P dV = 0. \quad (4.48)$$

Substituting the Van der Waals equation for P ,

$$P = \frac{RT}{V-b} - \frac{a}{V^2}, \quad (4.49)$$

the equation becomes

$$C_V dT + \frac{RT}{V-b} dV = 0. \quad (4.50)$$

Integration

Rearranging,

$$\frac{dT}{T} = -\frac{R}{C_V} \frac{dV}{V-b}. \quad (4.51)$$

Integrating,

$$\ln T = -\frac{R}{C_V} \ln(V-b) + \text{constant}. \quad (4.52)$$

Hence,

$$T(V-b)^{\frac{R}{C_V}} = \text{constant}. \quad (4.53)$$

Using the equation of state, the adiabatic condition can also be expressed as

$$\boxed{\left(P + \frac{a}{V^2} \right) (V-b)^{1+(R/C_V)} = \text{constant}.} \quad (4.54)$$

4.4.3 Relation Between Adiabatic and Isothermal Elasticity

For a gas, the relevant elastic constant is the *bulk modulus*, defined as the ratio of stress to strain:

$$E = \frac{\text{stress}}{\text{strain}} = -V \left(\frac{\partial P}{\partial V} \right). \quad (4.55)$$

Depending on the thermodynamic condition, two elastic moduli can be defined.

Isothermal Elasticity

For an isothermal process,

$$PV = \text{constant}. \quad (4.56)$$

Differentiating,

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{P}{V}. \quad (4.57)$$

Hence, the isothermal elastic modulus is

$$E_T = -V \left(\frac{\partial P}{\partial V}\right)_T = PV. \quad (4.58)$$

Adiabatic Elasticity

For an adiabatic process,

$$PV^\gamma = \text{constant}, \quad (4.59)$$

where $\gamma = C_P/C_V$.

Differentiating,

$$\left(\frac{\partial P}{\partial V}\right)_S = -\gamma \frac{P}{V}. \quad (4.60)$$

Thus, the adiabatic elastic modulus becomes

$$E_S = -V \left(\frac{\partial P}{\partial V}\right)_S = \gamma PV. \quad (4.61)$$

Ratio of Elasticities

The ratio of adiabatic to isothermal elasticity is therefore

$$\boxed{\frac{E_S}{E_T} = \gamma = \frac{C_P}{C_V}} \quad (4.62)$$

Chapter 5

Second Law of Thermodynamics

5.1 Heat Engine

An Idealised Heat Engine works by taking in a certain amount of heat Q_H , from a heat source, converting a portion of it to work W , and dumping the remaining heat Q_C into the heat sink.

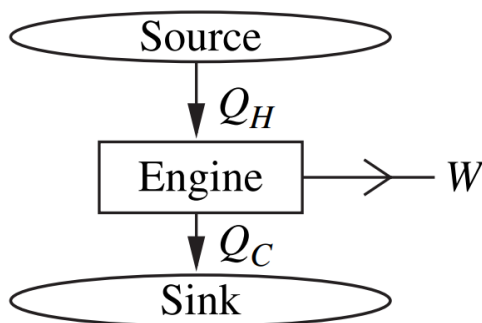


Figure 5.1: Heat Engine

Energy conservation (1st law of thermodynamics):

$$Q_H = W + Q_C \quad (5.1)$$

We Quantify the goodness of engine by how efficiently its working W by getting heat Q_H :

$$\text{Efficiency: } \eta = \frac{W}{Q_H} \quad (5.2)$$

5.2 Refrigerator

An idealised refrigerator is like a heat engine running back word.

We Work W on the refrigerator, so that it can take heat Q_c from cold system, and dumping heat Q_H at a higher temperature.

Similary, from 1st law of thermodynamics:

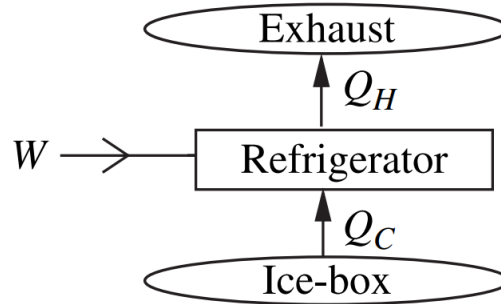


Figure 5.2: Refrigerator

$$W + Q_C = Q_H \quad (5.3)$$

We Quantify the goodness of refrigerator by its performance by taking heat from the cold system Q_C by working W on it.

$$\text{Performance: } \omega = \frac{Q_C}{W} \quad (5.4)$$

5.3 2nd Law of Thermodynamics

✓ 2nd law

Kelvin's statement

No process is possible, whose sole result is the complete conversion of heat into work.

Clausius's statement

No process is possible, whose sole result is the transfer of heat from a colder to a hotter body.

5.3.1 Anti-clausius Engine is equivalent to Anti-Kelvin Engine

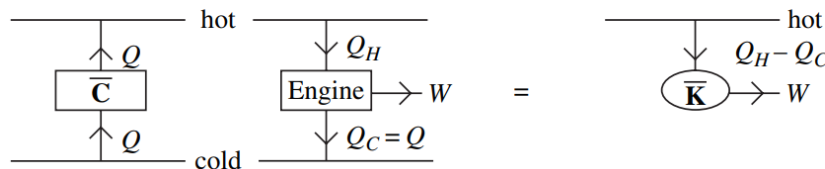


Figure 5.3: Anti-clausius Engine is equivalent to Anti-Kelvin Engine

Lets consider an Anti-clausius Engine, that takes Q heat from a colder body and transfer it Q completely to a hotter body.

Consider a heat engine, that takes Q_H heat from the same hot body and works W so that it can sink heat $Q_c = Q$ to the same cold body.

If we see these two systems (engine) combinely, than total heat taken from the hot body will be $Q_H - Q$ and total work done will be W . and there is no heat sinked to the cold body.

the combined system = anti-Clausius + heat engine, behaves like a Anti-Kelvin engine. that converts all heat $Q_H - Q$ to work W .

5.3.2 Anti-Kelvin Engine is equivalent to Anti-clausius Engine

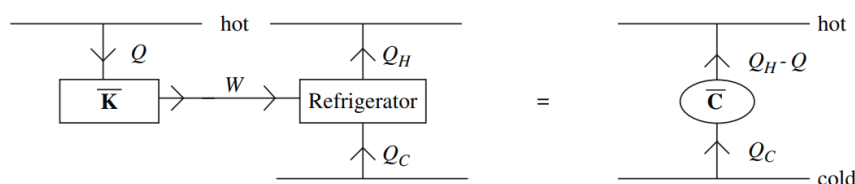


Figure 5.4: Anti-Kelvin Engine is equivalent to Anti-clausius Engine

Lets consider an anti-kelvin engine, that takes Q heat from a hot body and complety convert it into work $W = Q$.

Connect this work $W = Q$ to a refrigerator, that takes Q_C heat from a cold body, and sink $Q + Q_C$ to the same hotter body.

Combinely this system (Anti-kelvin + refrigerator), takes heat Q_c from a cold body and transfer compleete $Q_C = Q_H - Q$ into the hot body. same as an anti-clausius engine would work.

we basically shown that violation of one statement is equivalent to voilating another statement.

both statements are equivalent.

5.4 Carnot Engine

A carnot engine is any engine that is reversible, runs in a cycle with all of its heat exchanges taking place at a source temperature T_H and a sink at T_C .

💡 Reversible Process

A reversible process is one that can be run backward in time by simply reversing its inputs and outputs

5.4.1 Carnot's Theorem

✅ Carnot's theorem

No Engine operating between two reservoirs (at Temperature T_H and T_C) is more efficient than a Carnot engine operating between them.

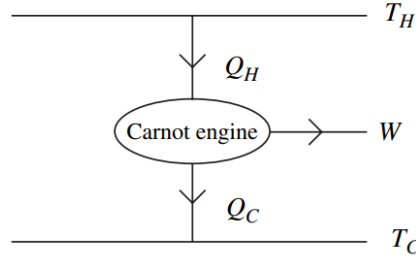


Figure 5.5: Carnot Engine

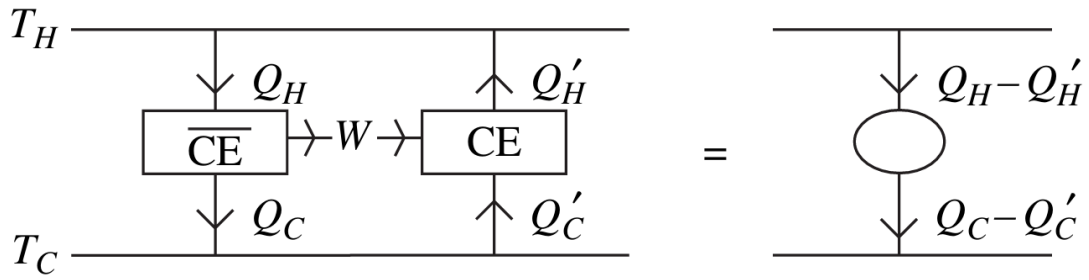


Figure 5.6: Illustrating the proof of carnot's theorem

Let say, we have a Carnot engine CE and one more engine \bar{CE} . Anti Carnot engine takes heat Q_H at Temperature T_H , works W and dumps Q_C at temperature T_C . (Working as a Heat Engine)

$$\eta_{\bar{CE}} = \frac{W}{Q_H} \quad (5.5)$$

Since carnot engine can run backward (reversibility), it takes Q'_C heat at temperature T_C and dump Q'_H heat at Temperature T_H . (Working as a refrigerator)

$$\eta_{CE} = \frac{W}{Q'_H} \quad (5.6)$$

This Combine system ($CE + \bar{CE}$) takes heat $Q_H - Q'_H$ at Temperature and dump heat $Q_C - Q'_C$ at Temperature T_C .

Energy Conservation:

$$Q_H - Q'_H = Q_C - Q'_C \quad (5.7)$$

By the Second Law of Thermodynamics:

If

$$T_H > T_C \quad (5.8)$$

Than

$$Q_H > Q'_H \quad \text{and} \quad Q_C > Q'_C \quad (5.9)$$

Which implies

$$\boxed{\eta_{CE} > \eta_{\bar{CE}}} \quad (5.10)$$

5.5 Temperature scale

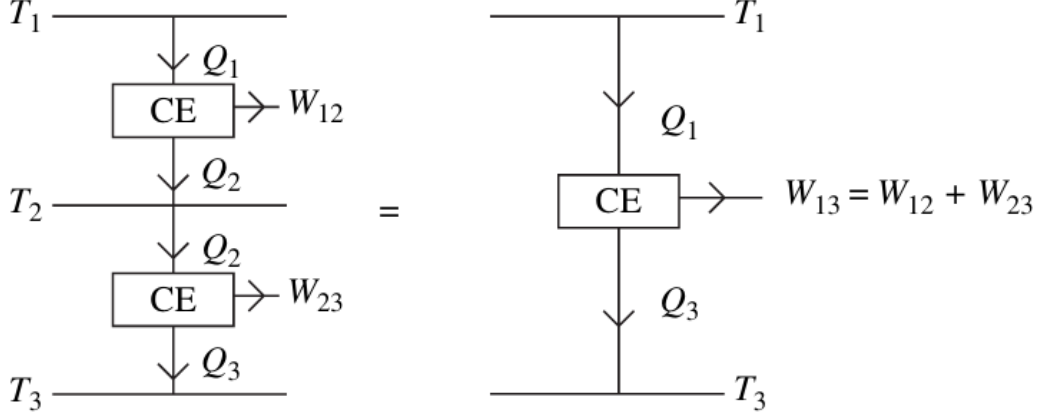


Figure 5.7: Connecting Two carnot engines

Energy conservation:

$$Q_2 = Q_1 - W_{12} = Q_1(1 - \eta(T_1, T_2)) \quad (5.11)$$

$$Q_3 = Q_2 - W_{23} = Q_2(1 - \eta(T_2, T_3)) = Q_1(1 - \eta(T_1, T_2))(1 - \eta(T_2, T_3)) \quad (5.12)$$

$$Q_3 = Q_1 - W_{13} = Q_1(1 - \eta(T_1, T_3)) \quad (5.13)$$

from 5.12 and 5.13,

$$[1 - \eta(T_1, T_2)][1 - \eta(T_2, T_3)] = [1 - \eta(T_1, T_3)] \quad (5.14)$$

To find the functional form of $\eta(T_H, T_C)$, We see from 5.14, Efficiency could be written as:

$$1 - \eta(T_1, T_2) = \frac{f(T_2)}{f(T_1)} \quad (5.15)$$

By convention, we set $\frac{f(T_2)}{f(T_1)} = \frac{T_2}{T_1}$ and hence $\eta(T_1, T_2) = 1 - \frac{T_2}{T_1}$ which implies the following:

$$\boxed{\eta(T_1, T_2) = 1 - \frac{T_2}{T_1} = 1 - \frac{Q_2}{Q_1}} \quad (5.16)$$

Or for a Carnot engine working between T_H (taking heat Q_H) and T_C (dumping heat Q_C)

$$\boxed{\eta(T_H, T_C) = 1 - \frac{T_H}{T_C} = 1 - \frac{Q_H}{Q_C}} \quad (5.17)$$

Chapter 6

Entropy

6.1 Clausius Theorem

✓ Clausius Theorem

For any cyclic transformation (reversible or irreversible),

$$\oint \frac{\delta Q}{T} \leq 0 \quad (6.1)$$

where δQ is the infinitesimal heat supplied to the system at absolute temperature T .

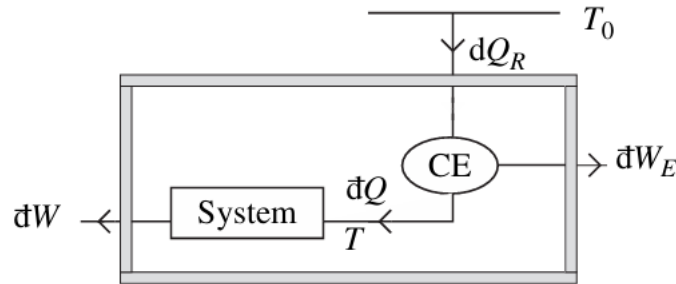


Figure 6.1: Illustration for Clausius theorem using a Carnot engine

Let us consider a Carnot engine working between two reservoirs at temperatures T_0 and T . The Carnot engine absorbs heat δQ_R from the reservoir at temperature T_0 and rejects heat δQ to a system at temperature T . Since the Carnot engine is reversible, it performs work δW_E .

For a reversible Carnot engine operating between temperatures T_0 and T ,

$$\frac{\delta Q_R}{\delta Q} = \frac{T_0}{T}. \quad (6.2)$$

Hence,

$$\delta Q_R = T_0 \frac{\delta Q}{T}. \quad (6.3)$$

The system at temperature T absorbs heat δQ from the Carnot engine and performs work δW .

Over a complete cycle, the total heat absorbed by the Carnot engine is

$$Q_R = T_0 \oint \frac{\delta Q}{T}. \quad (6.4)$$

Now consider the *combined system*, consisting of the original system and the Carnot engine together. This combined system absorbs heat Q_R from the single reservoir at temperature T_0 and converts it entirely into work W' , where

$$Q_R = W'. \quad (6.5)$$

This appears to violate the second law of thermodynamics (Kelvin–Planck statement), which forbids the complete conversion of heat from a single reservoir into work.

To ensure consistency with the second law, we must have

$$Q_R \leq 0. \quad (6.6)$$

Using Eqs. (6.4) and (6.6), and noting that $T_0 > 0$, we obtain

$$\boxed{\oint \frac{\delta Q}{T} \leq 0} \quad (6.7)$$

This proves Clausius theorem.

6.2 Consequences of Clausius Theorem

Clausius theorem states that for any cyclic process,

$$\oint \frac{\delta Q}{T} \leq 0. \quad (6.8)$$

This result has several important consequences.

6.2.1 Reversible Cyclic Process

For a *reversible* cyclic process, there is no dissipation and no entropy production. Hence the inequality becomes an equality:

$$\oint \frac{\delta Q_{\text{rev}}}{T} = 0. \quad (6.9)$$

This result is crucial, because it suggests that for reversible processes the quantity $\delta Q_{\text{rev}}/T$ behaves in a special way.

6.2.2 Irreversible Cyclic Process

For an *irreversible* cyclic process, dissipation is always present (for example due to friction, finite temperature gradients, etc.). In this case,

$$\oint \frac{\delta Q}{T} < 0. \quad (6.10)$$

Thus, the inequality in Clausius theorem distinguishes between reversible and irreversible processes.

6.2.3 Path Independence for Reversible Processes

Consider two equilibrium states A and B , connected by two different reversible paths R_1 and R_2 . Form a closed cycle by going from A to B along R_1 and returning from B to A along R_2 (in reverse direction).

Applying Eq. (6.9) to this reversible cycle,

$$\oint \frac{\delta Q_{\text{rev}}}{T} = \int_A^B \frac{\delta Q_{\text{rev}}}{T} \Big|_{R_1} + \int_B^A \frac{\delta Q_{\text{rev}}}{T} \Big|_{R_2} = 0. \quad (6.11)$$

Therefore,

$$\int_A^B \frac{\delta Q_{\text{rev}}}{T} \Big|_{R_1} = \int_A^B \frac{\delta Q_{\text{rev}}}{T} \Big|_{R_2}. \quad (6.12)$$

This shows that for reversible processes, the integral $\int \delta Q_{\text{rev}}/T$ depends only on the initial and final states, and not on the path.

6.3 Entropy

The result obtained above suggests the existence of a new thermodynamic state function.

Since the integral

$$\int_A^B \frac{\delta Q_{\text{rev}}}{T} \quad (6.13)$$

has the same value for all reversible paths connecting two equilibrium states A and B , it must correspond to the change of some state function.

This state function is called *entropy*.

6.3.1 Definition of Entropy

Entropy, denoted by S , is defined such that its infinitesimal change is

$$dS \equiv \frac{\delta Q_{\text{rev}}}{T}. \quad (6.14)$$

For a finite reversible process between states A and B ,

$$S(B) - S(A) = \int_A^B \frac{\delta Q_{\text{rev}}}{T}. \quad (6.15)$$

Thus, entropy is a *state function*, depending only on the equilibrium state of the system.

6.4 Entropy Change for Irreversible Processes

Consider an irreversible process that takes a system from an equilibrium state A to another equilibrium state B . Let the system return from B to A along a reversible path.

Together, these two processes form a closed thermodynamic cycle. According to Clausius theorem, for any cyclic process,

$$\oint \frac{\delta Q}{T} \leq 0. \quad (6.16)$$

The cyclic integral may be expressed as the sum of the integrals over the two paths:

$$\oint \frac{\delta Q}{T} = \int_A^B \frac{\delta Q}{T} + \int_B^A \frac{\delta Q_{\text{rev}}}{T}. \quad (6.17)$$

Since reversing the limits of integration changes the sign,

$$\int_B^A \frac{\delta Q_{\text{rev}}}{T} = - \int_A^B \frac{\delta Q_{\text{rev}}}{T}, \quad (6.18)$$

we obtain

$$\int_A^B \frac{\delta Q}{T} \leq \int_A^B \frac{\delta Q_{\text{rev}}}{T}. \quad (6.19)$$

The equality holds only if the entire cycle is reversible. Since the path from A to B is irreversible, the inequality is strict.

Using the definition of entropy,

$$S(B) - S(A) = \int_A^B \frac{\delta Q_{\text{rev}}}{T}, \quad (6.20)$$

we finally obtain

$$\int_A^B \frac{\delta Q}{T} < S(B) - S(A). \quad (6.21)$$

In differential form, this may be written as

$$\boxed{dS > \frac{\delta Q}{T}} \quad (6.22)$$

This inequality provides a general mathematical statement of the second law of thermodynamics for irreversible processes.

6.5 Entropy Change for an Isolated System

An isolated system does not exchange heat with its surroundings. Hence,

$$\delta Q = 0. \quad (6.23)$$

From the entropy inequality,

$$dS \geq \frac{\delta Q}{T}, \quad (6.24)$$

it follows immediately that

$$dS \geq 0. \quad (6.25)$$

Thus, the entropy of an isolated system can never decrease. It remains constant for reversible processes and increases for irreversible processes.

This result introduces a natural direction (or *arrow*) to thermodynamic processes.

6.5.1 Principle of Increase of Entropy

The behavior of entropy in isolated systems leads to a fundamental statement of the second law of thermodynamics.

✓ Principle of Increase of Entropy

The entropy of an isolated system can never decrease:

$$\Delta S \geq 0. \quad (6.26)$$

The equality holds for reversible processes, while the inequality holds for irreversible processes.

6.5.2 Reversible and Irreversible Processes

- **Reversible process:** For a reversible process occurring in an isolated system,

$$\Delta S = 0. \quad (6.27)$$

The entropy of the system remains constant.

- **Irreversible process:** For an irreversible process occurring in an isolated system,

$$\Delta S > 0. \quad (6.28)$$

The entropy of the system increases.

Hence, entropy production provides a quantitative measure of irreversibility in a thermodynamic process.

💡 Arrow of Time

The principle of increase of entropy introduces a preferred direction to physical processes. While the laws of mechanics are time-reversible, thermodynamic processes are not.

Spontaneous processes in an isolated system always proceed in the direction of increasing entropy.

6.5.3 Entropy and Equilibrium

For an isolated system in thermodynamic equilibrium,

$$dS = 0. \quad (6.29)$$

Any small spontaneous deviation from equilibrium leads to a decrease of entropy,

$$d^2S < 0. \quad (6.30)$$

Therefore, the equilibrium state of an isolated system corresponds to a state of *maximum entropy*.

💡 Maximum Entropy Principle

Thermodynamic equilibrium in an isolated system is characterized by maximum entropy. This principle provides the final criterion for equilibrium and stability.

6.6 First Law Revisited: Entropy Representation

We now return to the first law of thermodynamics and reformulate it using the concept of entropy.

The first law for an infinitesimal process is

$$\delta Q = dU + \delta W. \quad (6.31)$$

For a reversible process, the heat absorbed by the system can be written in terms of entropy as

$$\delta Q_{\text{rev}} = T dS. \quad (6.32)$$

Substituting this into the first law, we obtain

$$T dS = dU + \delta W_{\text{rev}}. \quad (6.33)$$

For a simple compressible system performing only $P dV$ work,

$$\delta W_{\text{rev}} = P dV. \quad (6.34)$$

Hence, the first law becomes

$$\boxed{dU = T dS - P dV} \quad (6.35)$$

This equation is the *fundamental thermodynamic relation* for a simple system.

6.6.1 Significance of the Entropy Formulation

The introduction of entropy allows heat, which is a path-dependent quantity, to be expressed in terms of exact differentials.

While δQ is not a state function, the quantity $\delta Q_{\text{rev}}/T$ is an exact differential:

$$dS = \frac{\delta Q_{\text{rev}}}{T}. \quad (6.36)$$

Thus, entropy provides a bridge between energy conservation (first law) and irreversibility (second law).

Unified View

The equation

$$dU = T dS - P dV$$

combines the first and second laws into a single mathematical statement.

Energy conservation determines *how much* energy changes, while entropy determines *how* the process can occur.

- The term $T dS$ represents the reversible heat exchange.
- The term $P dV$ represents mechanical work.

Chapter 7

Thermodynamic Potentials

7.1 Internal Energy U

As introduced in Chapter 4, the internal energy U represents the total energy of a thermodynamic system.

In the most general form, the first law of thermodynamics may be written as

$$dU = T dS + J \cdot dx + \mu dN, \quad (7.1)$$

where S is the entropy, x is a generalized displacement with conjugate generalized force J , and N is the number of particles with chemical potential μ .

Equation (7.1) implies that the internal energy is a function of the extensive variables S , x , and N :

$$U = U(S, x, N). \quad (7.2)$$

From Eq. (7.1), the corresponding thermodynamic derivatives are

$$\left(\frac{\partial U}{\partial S}\right)_{x,N} = T, \quad \left(\frac{\partial U}{\partial x}\right)_{S,N} = J, \quad \left(\frac{\partial U}{\partial N}\right)_{S,x} = \mu. \quad (7.3)$$

For fixed intensive variables (T, J, μ) , all extensive quantities are proportional to the size of the system.

7.1.1 Gibbs–Duhem Relation

Internal energy is an extensive quantity. Therefore, if the size of the system is increased by a factor λ , all extensive variables scale by the same factor:

$$U(\lambda S, \lambda x, \lambda N) = \lambda U(S, x, N). \quad (7.4)$$

Differentiating both sides with respect to λ , we obtain

$$\frac{\partial U}{\partial(\lambda S)} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda x)} \frac{\partial(\lambda x)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda N)} \frac{\partial(\lambda N)}{\partial \lambda} = U(S, x, N). \quad (7.5)$$

Using

$$\frac{\partial U}{\partial S} = T, \quad \frac{\partial U}{\partial x} = J, \quad \frac{\partial U}{\partial N} = \mu,$$

and setting $\lambda = 1$, we obtain

$$\boxed{U = TS + J \cdot x + \mu \cdot N} \quad (7.6)$$

Equation (7.6) shows that

💡 Internal Energy

the internal energy consists of three contributions: thermal energy TS , mechanical work energy $J \cdot x$, and chemical potential energy $\mu \cdot N$.

Taking the total differential of Eq. (7.6), we obtain

$$dU = T dS + S dT + J \cdot dx + x \cdot dJ + \mu dN + N \cdot d\mu. \quad (7.7)$$

Comparing Eq. (7.7) with the first law in Eq. (7.1), we obtain

$$\boxed{S dT + x \cdot dJ + N \cdot d\mu = 0} \quad (7.8)$$

This relation is known as the *Gibbs–Duhem relation*. It expresses the dependence between the intensive variables T , J , and μ , and is a direct consequence of the extensivity of internal energy.

7.1.2 Maxwell's First Relation

For simplicity, we now consider a simple compressible system:

$$\boxed{dU = T dS - P dV} \quad (7.9)$$

Hence, internal energy is a function of entropy and volume:

$$U = U(S, V). \quad (7.10)$$

From this relation,

$$T = \left(\frac{\partial U}{\partial S} \right)_V, \quad -P = \left(\frac{\partial U}{\partial V} \right)_S. \quad (7.11)$$

Since $U(S, V)$ is a well-defined state function, the mixed second derivatives must be equal:

$$\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right)_V = \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right)_S. \quad (7.12)$$

Substituting the thermodynamic derivatives, we obtain

$$\boxed{\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V} \quad (7.13)$$

This equation is known as the *first Maxwell relation*. It follows directly from the exactness of the differential dU and is independent of the microscopic nature of the system.

7.2 Enthalpy H

For an isolated system, the entropy must increase during any spontaneous process and reaches a maximum in equilibrium. This provides the equilibrium criterion when no exchange with the surroundings is allowed.

However, many physical systems are *not* isolated. They may exchange mechanical work with their surroundings, such as pressure–volume work. In such situations, entropy alone is no longer the most convenient quantity for describing equilibrium.

Consider a system that can perform mechanical work of the form $J \cdot dx$ (for example, pressure–volume work $P dV$) while remaining thermally insulated ($\delta Q = 0$).

For such systems, it is useful to introduce a new thermodynamic potential that naturally incorporates mechanical work. This potential is called *enthalpy*.

7.2.1 Definition of Enthalpy

Enthalpy H is defined as

$$H = U - J \cdot x. \quad (7.14)$$

For the simple compressible systems of interest, where

$$J = -P, \quad x = V,$$

the enthalpy becomes

$$\boxed{H = U + PV} \quad (7.15)$$

Enthalpy

Thus, enthalpy represents the total energy required to create the system and make room for it against an external pressure.

7.2.2 Maxwell's Second relation

Taking the total differential of $H = U + PV$, we obtain

$$dH = dU + P dV + V dP. \quad (7.16)$$

Using the fundamental thermodynamic relation

$$dU = T dS - P dV, \quad (7.17)$$

we substitute into the above equation to obtain

$$\boxed{dH = T dS + V dP} \quad (7.18)$$

This expression shows that enthalpy is naturally a function of entropy and pressure:

$$H = H(S, P). \quad (7.19)$$

From the differential form of enthalpy,

$$dH = T dS + V dP, \quad (7.20)$$

we identify

$$T = \left(\frac{\partial H}{\partial S} \right)_P, \quad V = \left(\frac{\partial H}{\partial P} \right)_S. \quad (7.21)$$

Since $H(S, P)$ is a state function, its mixed second derivatives must be equal:

$$\frac{\partial}{\partial P} \left(\frac{\partial H}{\partial S} \right)_P = \frac{\partial}{\partial S} \left(\frac{\partial H}{\partial P} \right)_S. \quad (7.22)$$

Substituting the thermodynamic derivatives, we obtain

$$\boxed{\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P} \quad (7.23)$$

This equation is known as the *second Maxwell relation*.

7.3 Helmholtz Free Energy F

Helmholtz free energy is the thermodynamic potential that is most useful for systems in contact with a heat reservoir at constant temperature T and fixed volume V .

In such cases, the natural control variables are T and V , and the equilibrium state corresponds to minimum Helmholtz free energy.

Helmholtz free Energy

Physically, F represents the amount of energy available to do useful work at constant temperature.

7.3.1 Definition of Helmholtz Free Energy

Helmholtz free energy is defined as

$$\boxed{F = U - TS} \quad (7.24)$$

This definition subtracts the energy “unavailable for work” due to entropy.

7.3.2 Maxwell’s Third relation

Taking the total differential, we get

$$dF = dU - T dS - S dT. \quad (7.25)$$

Using the fundamental relation $dU = T dS - P dV$, we obtain

$$dF = -P dV - S dT. \quad (7.26)$$

we see that the natural variables of Helmholtz free energy are

$$F = F(T, V). \quad (7.27)$$

Consequently,

$$S = - \left(\frac{\partial F}{\partial T} \right)_V, \quad P = - \left(\frac{\partial F}{\partial V} \right)_T. \quad (7.28)$$

Since $F(T, V)$ is a state function, its mixed second derivatives are equal:

$$\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T} \right)_V = \frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V} \right)_T. \quad (7.29)$$

Substituting the thermodynamic derivatives, we obtain the Maxwell relation:

$$\boxed{\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V} \quad (7.30)$$

This is the Maxwell relation associated with Helmholtz free energy.

7.4 Gibbs Free Energy G

Gibbs free energy is the thermodynamic potential most useful for systems in contact with a heat and pressure reservoir, i.e., at constant temperature T and constant pressure P .

In such situations, the equilibrium state corresponds to minimum Gibbs free energy.



Gibbs Free Energy

Physically, G represents the maximum useful (non- $P dV$) work that a system can perform when the temperature and pressure are held constant.

7.4.1 Definition of Gibbs Free Energy

Gibbs free energy is defined as

$$\boxed{G = U + PV - TS} \quad (7.31)$$

Equivalently, using $H = U + PV$,

$$G = H - TS \quad (7.32)$$

7.4.2 Maxwell's Fourth relation

Taking the total differential, we have

$$dG = dU + P dV + V dP - T dS - S dT. \quad (7.33)$$

Using the fundamental relation $dU = T dS - P dV$, we simplify:

$$dG = -S dT + V dP \quad (7.34)$$

From the differential, it is clear that the natural variables of Gibbs free energy are

$$G = G(T, P) \quad (7.35)$$

Correspondingly, the thermodynamic derivatives are

$$S = - \left(\frac{\partial G}{\partial T} \right)_P, \quad V = \left(\frac{\partial G}{\partial P} \right)_T \quad (7.36)$$

Since $G(T, P)$ is a state function, its mixed second derivatives are equal:

$$\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T} \right)_P = \frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P} \right)_T \quad (7.37)$$

Substituting the thermodynamic derivatives, we obtain the Maxwell relation:

$$\boxed{\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P} \quad (7.38)$$

This is the Maxwell relation associated with Gibbs free energy.

Chapter 8

Thermodynamic relations

8.1 The $T dS$ Equations

Entropy is a state function and may be expressed in terms of different pairs of independent thermodynamic variables. Depending on the choice of variables, different forms of the $T dS$ equation are obtained. We derive all three standard forms below.

8.1.1 Entropy as a Function of T and V

Let the entropy be expressed as

$$S = S(T, V). \quad (8.1)$$

The total differential of entropy is

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV. \quad (8.2)$$

Multiplying throughout by T ,

$$T dS = T \left(\frac{\partial S}{\partial T} \right)_V dT + T \left(\frac{\partial S}{\partial V} \right)_T dV. \quad (8.3)$$

From the definition of heat capacity at constant volume,

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V, \quad (8.4)$$

and using the Maxwell relation

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V, \quad (8.5)$$

we obtain

$$\boxed{T dS = C_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV.} \quad (8.6)$$

This is the first $T dS$ equation.

8.1.2 Entropy as a Function of T and P

Let entropy be written as

$$S = S(T, P). \quad (8.7)$$

The total differential is

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP. \quad (8.8)$$

Multiplying by T ,

$$T dS = T \left(\frac{\partial S}{\partial T} \right)_P dT + T \left(\frac{\partial S}{\partial P} \right)_T dP. \quad (8.9)$$

Using the definition of heat capacity at constant pressure,

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P, \quad (8.10)$$

and the Maxwell relation

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P, \quad (8.11)$$

we obtain

$$\boxed{T dS = C_P dT - T \left(\frac{\partial V}{\partial T} \right)_P dP.} \quad (8.12)$$

This is the second $T dS$ equation.

8.1.3 Entropy as a Function of P and V

Let entropy be expressed as

$$S = S(P, V). \quad (8.13)$$

The total differential is

$$dS = \left(\frac{\partial S}{\partial P} \right)_V dP + \left(\frac{\partial S}{\partial V} \right)_P dV. \quad (8.14)$$

Multiplying by T ,

$$T dS = T \left(\frac{\partial S}{\partial P} \right)_V dP + T \left(\frac{\partial S}{\partial V} \right)_P dV. \quad (8.15)$$

Using thermodynamic identities,

$$T \left(\frac{\partial S}{\partial P} \right)_V = C_V \left(\frac{\partial T}{\partial P} \right)_V, \quad (8.16)$$

$$T \left(\frac{\partial S}{\partial V} \right)_P = C_P \left(\frac{\partial T}{\partial V} \right)_P, \quad (8.17)$$

we obtain

$$\boxed{T dS = C_V \left(\frac{\partial T}{\partial P} \right)_V dP + C_P \left(\frac{\partial T}{\partial V} \right)_P dV.} \quad (8.18)$$

This is the third $T dS$ equation.

8.2 Clapeyron Equation

The Clapeyron equation describes the slope of a phase boundary in the pressure–temperature (P – T) diagram. It is derived from the condition of thermodynamic equilibrium between two coexisting phases.

Thermodynamic Condition for Phase Equilibrium

Consider a system in which two phases, denoted by α and β , coexist in equilibrium. The necessary and sufficient condition for phase equilibrium is the equality of chemical potentials:

$$\mu^{(\alpha)}(T, P) = \mu^{(\beta)}(T, P). \quad (8.19)$$

Along the phase coexistence curve, this equality must hold for infinitesimal changes in T and P . Hence,

$$d\mu^{(\alpha)} = d\mu^{(\beta)}. \quad (8.20)$$

Differential of Chemical Potential

For a simple compressible system, the differential of chemical potential is given by

$$d\mu = -S_m dT + V_m dP, \quad (8.21)$$

where S_m and V_m are the molar entropy and molar volume, respectively.

Applying this to the two phases,

$$d\mu^{(\alpha)} = -S_m^{(\alpha)} dT + V_m^{(\alpha)} dP, \quad (8.22)$$

$$d\mu^{(\beta)} = -S_m^{(\beta)} dT + V_m^{(\beta)} dP. \quad (8.23)$$

Since $d\mu^{(\alpha)} = d\mu^{(\beta)}$, we obtain

$$[S_m^{(\beta)} - S_m^{(\alpha)}] dT = [V_m^{(\beta)} - V_m^{(\alpha)}] dP. \quad (8.24)$$

Clapeyron Equation

Rearranging the above relation,

$$\boxed{\frac{dP}{dT} = \frac{S_m^{(\beta)} - S_m^{(\alpha)}}{V_m^{(\beta)} - V_m^{(\alpha)}}} \quad (8.25)$$

Using the definition of latent heat per mole,

$$L = T (S_m^{(\beta)} - S_m^{(\alpha)}), \quad (8.26)$$

the Clapeyron equation can be written in the standard form

$$\boxed{\frac{dP}{dT} = \frac{L}{T (V_m^{(\beta)} - V_m^{(\alpha)})}} \quad (8.27)$$

This is the *Clapeyron equation*. It is valid for all first-order phase transitions such as solid–liquid, liquid–vapour, and solid–vapour equilibrium.

8.2.1 Clausius–Clapeyron Equation (Liquid–Vapour Transition)

For a liquid–vapour phase transition,

$$V_m^{(v)} \gg V_m^{(l)}. \quad (8.28)$$

Hence,

$$V_m^{(v)} - V_m^{(l)} \approx V_m^{(v)}. \quad (8.29)$$

Assuming the vapour behaves as an ideal gas,

$$V_m^{(v)} = \frac{RT}{P}. \quad (8.30)$$

Substituting into the Clapeyron equation,

$$\frac{dP}{dT} = \frac{L}{T} \cdot \frac{P}{RT} \quad (8.31)$$

$$= \frac{LP}{RT^2}. \quad (8.32)$$

Rearranging,

$$\boxed{\frac{dP}{P} = \frac{L}{RT^2} dT} \quad (8.33)$$

This is the *Clausius–Clapeyron equation* in differential form.

Integrated Clausius–Clapeyron Equation

If the latent heat L is assumed to be temperature independent, integration yields

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{L}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}. \quad (8.34)$$

Performing the integrations,

$$\boxed{\ln \left(\frac{P_2}{P_1} \right) = -\frac{L}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)} \quad (8.35)$$

This form is widely used to determine latent heat from vapour pressure data.

8.3 Joule–Thomson Expansion

The Joule–Thomson effect refers to the change in temperature of a real gas when it is forced to expand from a region of high pressure to a region of low pressure through a porous plug or throttle valve under adiabatic conditions. Since the system is thermally insulated, no heat is exchanged with the surroundings during the process.

Such an expansion is commonly known as *throttling expansion*. The Joule–Thomson effect is of fundamental importance in refrigeration, liquefaction of gases, and cryogenic applications.

For most real gases at ordinary temperatures, the gas cools upon expansion. However, gases such as hydrogen and helium exhibit heating under similar conditions unless they are cooled below a characteristic temperature called the *inversion temperature*.

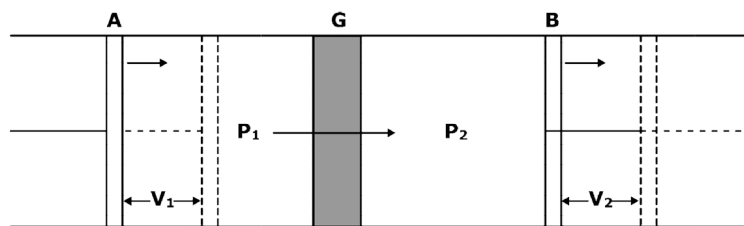


Figure 8.1: The porous experiment

8.3.1 Isoenthalpic Nature of Joule–Thomson Expansion

Consider a gas flowing steadily through a porous plug from an initial state (P_1, V_1, T_1) to a final state (P_2, V_2, T_2) in an insulated tube.

The work done on the gas at the inlet is

$$W_1 = P_1 V_1, \quad (8.36)$$

and the work done by the gas at the outlet is

$$W_2 = P_2 V_2. \quad (8.37)$$

Since the process is adiabatic and no macroscopic kinetic energy change is involved, the first law of thermodynamics gives

$$U_2 - U_1 = P_1 V_1 - P_2 V_2. \quad (8.38)$$

Rearranging,

$$U_1 + P_1 V_1 = U_2 + P_2 V_2. \quad (8.39)$$

Using the definition of enthalpy $H = U + PV$, we obtain

$$H_1 = H_2, \quad (8.40)$$

or

$$\boxed{\Delta H = 0.} \quad (8.41)$$

Thus, Joule–Thomson expansion is an *isoenthalpic* process.

8.3.2 Joule–Thomson Coefficient

The *Joule–Thomson coefficient* μ_{JT} is defined as

$$\boxed{\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H} \quad (8.42)$$

The quantity μ_{JT} is called the *Joule–Thomson coefficient*. It represents the rate of change of temperature with pressure during an isoenthalpic process.

- $\mu_{JT} > 0$: cooling on expansion
- $\mu_{JT} < 0$: heating on expansion

- $\mu_{JT} = 0$: no temperature change

Since enthalpy is a function of temperature and pressure, we write

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP. \quad (8.43)$$

Using the thermodynamic identity

$$\left(\frac{\partial H}{\partial T} \right)_P = C_P, \quad (8.44)$$

the above equation becomes

$$dH = C_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP. \quad (8.45)$$

For a Joule–Thomson process, $dH = 0$, hence

$$C_P dT = - \left(\frac{\partial H}{\partial P} \right)_T dP. \quad (8.46)$$

Therefore,

$$\boxed{\mu_{JT} \equiv \left(\frac{\partial T}{\partial P} \right)_H = - \frac{1}{C_P} \left(\frac{\partial H}{\partial P} \right)_T.} \quad (8.47)$$

Evaluation of $\left(\frac{\partial H}{\partial P} \right)_T$

Starting from the thermodynamic identity,

$$dH = T dS + V dP, \quad (8.48)$$

we write entropy as $S(T, P)$:

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP.$$

Substituting,

$$dH = T \left(\frac{\partial S}{\partial T} \right)_P dT + \left[V + T \left(\frac{\partial S}{\partial P} \right)_T \right] dP. \quad (8.49)$$

Thus,

$$\left(\frac{\partial H}{\partial P} \right)_T = V + T \left(\frac{\partial S}{\partial P} \right)_T. \quad (8.50)$$

Using the Maxwell relation,

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P, \quad (8.51)$$

we get

$$\left(\frac{\partial H}{\partial P} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_P. \quad (8.52)$$

the Joule–Thomson coefficient may be written as

$$\boxed{\mu_{JT} \equiv \left(\frac{\partial T}{\partial P} \right)_H = - \frac{1}{C_P} \left(\frac{\partial H}{\partial P} \right)_T = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right].} \quad (8.53)$$

8.3.3 Ideal Gas Case

For an ideal gas,

$$V = \frac{nRT}{P}, \quad \left(\frac{\partial V}{\partial T} \right)_P = \frac{nR}{P}.$$

Substituting,

$$\mu_{JT} = \frac{1}{C_P} \left(\frac{nRT}{P} - \frac{nRT}{P} \right) = 0.$$

8.3.4 Joule–Thomson Coefficient for van der Waals

For one mole of a van der Waals gas,

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT. \quad (8.54)$$

For low pressures, neglecting higher-order terms,

$$V \approx \frac{RT}{P} + b - \frac{a}{RT}. \quad (8.55)$$

Differentiating with respect to T at constant P ,

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P} + \frac{a}{RT^2}. \quad (8.56)$$

Substituting into the expression for μ_{JT} ,

$$\mu_{JT} = \frac{1}{C_P} \left(\frac{2a}{RT} - b \right). \quad (8.57)$$

Inversion Temperature

The inversion temperature T_i is defined as the temperature at which the Joule–Thomson coefficient changes sign, i.e.,

$$\mu_{JT} = 0. \quad (8.58)$$

From the above expression,

$$\frac{2a}{RT_i} = b, \quad (8.59)$$

which gives

$$\boxed{T_i = \frac{2a}{Rb}}. \quad (8.60)$$

For $T < T_i$, the gas cools on expansion ($\mu_{JT} > 0$), while for $T > T_i$, the gas heats up ($\mu_{JT} < 0$).

Chapter 9

Third Law of Thermodynamics

The first and second laws of thermodynamics introduce the concepts of energy conservation and entropy, but they do not fix the *absolute value* of entropy. The third law provides this missing reference by specifying the behavior of entropy as the temperature approaches absolute zero.

This law plays a crucial role in low-temperature physics, chemical thermodynamics, and the definition of absolute entropy.

From the second law, entropy is defined through

$$dS = \frac{\delta Q_{\text{rev}}}{T}. \quad (9.1)$$

This definition determines only *changes* in entropy. To assign an absolute value of entropy, a reference state is required. The third law supplies this reference by specifying the entropy at absolute zero.

9.1 Statement of the Third Law

✓ Third Law of Thermodynamics (Planck Statement)

The entropy of a perfect crystalline substance approaches zero as the temperature approaches absolute zero:

$$\lim_{T \rightarrow 0} S = 0 \quad (9.2)$$

A *perfect crystal* is one with a unique ground state (no residual disorder).

9.2 Mathematical Formulation

At constant volume, the reversible heat supplied to a system is

$$\delta Q_{\text{rev}} = C_V(T) dT, \quad (9.3)$$

where C_V is the heat capacity at constant volume.

Hence,

$$dS = \frac{C_V(T)}{T} dT. \quad (9.4)$$

Integrating from absolute zero to temperature T ,

$$S(T) - S(0) = \int_0^T \frac{C_V(T')}{T'} dT' \quad (9.5)$$

This equation is the central mathematical expression underlying the third law.

9.3 Vanishing of Heat Capacity at Absolute Zero

For the entropy at $T = 0$ to be finite, the integral in Eq. (9.5) must converge. This requires

$$\lim_{T \rightarrow 0} C_V(T) = 0 \quad (9.6)$$

Thus, the third law implies that the heat capacity of all systems must vanish as the temperature approaches absolute zero.

💡 Physical Meaning

At very low temperatures, thermal motion freezes out and the system cannot absorb energy efficiently, leading to vanishing heat capacity.

9.4 Zero Entropy of a Perfect Crystal

From statistical mechanics, entropy is given by Boltzmann's formula:

$$S = k_B \ln W, \quad (9.7)$$

where W is the number of accessible microstates.

For a perfect crystal at $T = 0$,

$$W = 1, \quad (9.8)$$

since the ground state is unique.

Hence,

$$S(0) = 0 \quad (9.9)$$

This provides a microscopic justification of the third law.

9.5 Nernst Heat Theorem

An alternative formulation of the third law is the *Nernst heat theorem*.

✅ Nernst Heat Theorem

The entropy change associated with any isothermal reversible process tends to zero as the temperature approaches absolute zero:

$$\lim_{T \rightarrow 0} \Delta S = 0 \quad (9.10)$$

Mathematical Justification

For an isothermal reversible process,

$$\Delta S = \int \frac{\delta Q_{\text{rev}}}{T}. \quad (9.11)$$

As $T \rightarrow 0$, the heat exchanged $\delta Q_{\text{rev}} \rightarrow 0$ due to vanishing heat capacity, hence $\Delta S \rightarrow 0$.

9.6 Independence of Entropy from External Parameters

Using Maxwell relations, one can show that

$$\left(\frac{\partial S}{\partial X} \right)_T = \left(\frac{\partial Y}{\partial T} \right)_X, \quad (9.12)$$

where X and Y are conjugate variables.

As $T \rightarrow 0$,

$$\left(\frac{\partial Y}{\partial T} \right)_X \rightarrow 0, \quad (9.13)$$

implying

$$\boxed{\left(\frac{\partial S}{\partial X} \right)_{T=0} = 0} \quad (9.14)$$

Thus, entropy at absolute zero is independent of pressure, volume, magnetic field, or other external parameters.

9.7 Unattainability of Absolute Zero

Another equivalent statement of the third law is the *unattainability principle*.

✓ Unattainability Principle

Absolute zero cannot be reached in a finite number of thermodynamic processes.

Mathematical Argument

A temperature change is given by

$$dT = \frac{\delta Q}{C(T)}. \quad (9.15)$$

As $T \rightarrow 0$, $C(T) \rightarrow 0$, so achieving a finite decrease in temperature requires an infinite number of steps.

9.8 Residual Entropy

If a system has a degenerate ground state ($W > 1$), then

$$S(0) = k_B \ln W \neq 0. \quad (9.16)$$

This is known as *residual entropy* and occurs in systems with frozen disorder, such as glasses.

Important Note

The third law strictly applies to *perfect crystals*. Residual entropy does not violate the law but reflects incomplete ordering.

The third law thus completes the logical structure of thermodynamics and provides the foundation for low-temperature physics.

Appendix A

The Polytropic Process

A polytropic process is a general thermodynamic path followed by an ideal gas that satisfies the mathematical relationship:

$$PV^x = \text{constant} \quad (\text{A.1})$$

where x is the polytropic index.

By varying the value of x , we recover the four fundamental processes:

Index (x)	Process Type	Mathematical Result	Physical Meaning
$x = 0$	Isobaric	$P = \text{const}$	Constant Pressure
$x = 1$	Isothermal	$PV = \text{const}$	Constant Temperature
$x = \gamma$	Adiabatic	$PV^\gamma = \text{const}$	No heat exchange ($Q = 0$)
$x = \infty$	Isochoric	$V = \text{const}$	Constant Volume

Table A.1:

Appendix B

Equation of states

B.1 Berthelot Equation of State

$$P = \frac{RT}{V_m - b} - \frac{a}{TV_m^2} \quad (\text{B.1})$$

Parameters:

- a : attraction parameter
- b : co-volume parameter

B.2 Clausius Equation of State

$$P = \frac{RT}{V_m - b} - \frac{a}{T(V_m + c)^2} \quad (\text{B.2})$$

Parameters:

- a : attraction constant
- b : excluded volume
- c : correction parameter accounting for molecular structure

B.3 Virial Equation of State

$$\frac{PV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \dots \quad (\text{B.3})$$

Parameters:

- $B(T)$: second virial coefficient (pair interactions)
- $C(T)$: third virial coefficient (three-body interactions)
- $D(T)$: higher-order interaction coefficients

B.4 Redlich–Kwong Equation of State

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}V_m(V_m + b)} \quad (\text{B.4})$$

Parameters:

- a : attraction parameter
- b : co-volume parameter

B.5 Soave–Redlich–Kwong (SRK) Equation

$$P = \frac{RT}{V_m - b} - \frac{a\alpha(T)}{V_m(V_m + b)} \quad (\text{B.5})$$

Parameters:

- a : attraction constant
- b : co-volume
- $\alpha(T)$: temperature-dependent correction factor

B.6 Peng–Robinson Equation of State

$$P = \frac{RT}{V_m - b} - \frac{a\alpha(T)}{V_m(V_m + b) + b(V_m - b)} \quad (\text{B.6})$$

Parameters:

- a : attraction parameter
- b : co-volume
- $\alpha(T)$: temperature correction function

B.7 Hard-Sphere Equation of State

$$Z = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (\text{B.7})$$

Parameters:

- Z : compressibility factor
- η : packing fraction

B.8 Benedict–Webb–Rubin (BWR) Equation

$$P = RT\rho + (B_0RT - A_0)\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 \quad (\text{B.8})$$

Parameters:

- A_0, B_0, a, b, α : empirical constants obtained from experiment

B.9 Degenerate Fermi Gas Equation of State

$$P = K\rho^{5/3} \quad (\text{B.9})$$

Parameters:

- K : constant depending on particle mass and Planck's constant

B.10 Bose Gas Equation of State

$$P = \frac{kT}{\lambda^3} g_{5/2}(z) \quad (\text{B.10})$$

Parameters:

- k : Boltzmann constant
- λ : thermal de Broglie wavelength
- $g_{5/2}(z)$: Bose–Einstein function
- z : fugacity

B.11 Radiation Equation of State

$$P = \frac{1}{3}aT^4 \quad (\text{B.11})$$

Parameters:

- a : radiation constant

Appendix C

Spherical Coordinate System

C.1 Definition of Spherical Coordinates

In the spherical coordinate system, the position of a point in space is specified by the coordinates (r, θ, ϕ) , where:

- r is the radial distance from the origin,
- θ is the polar angle measured from the positive z -axis ($0 \leq \theta \leq \pi$),
- ϕ is the azimuthal angle measured in the xy -plane from the positive x -axis ($0 \leq \phi < 2\pi$).

The transformation between Cartesian and spherical coordinates is given by

$$x = r \sin \theta \cos \phi, \quad (\text{C.1})$$

$$y = r \sin \theta \sin \phi, \quad (\text{C.2})$$

$$z = r \cos \theta. \quad (\text{C.3})$$

Conversely,

$$r = \sqrt{x^2 + y^2 + z^2}, \quad (\text{C.4})$$

$$\theta = \cos^{-1} \left(\frac{z}{r} \right), \quad (\text{C.5})$$

$$\phi = \tan^{-1} \left(\frac{y}{x} \right). \quad (\text{C.6})$$

C.2 Unit Vectors in Spherical Coordinates

The spherical coordinate system uses three mutually orthogonal unit vectors:

- $\hat{\mathbf{r}}$ in the radial direction,
- $\hat{\boldsymbol{\theta}}$ in the direction of increasing θ ,
- $\hat{\boldsymbol{\phi}}$ in the direction of increasing ϕ .

These unit vectors vary with position and are related to the Cartesian unit vectors by

$$\hat{\mathbf{r}} = \sin \theta \cos \phi \hat{\mathbf{x}} + \sin \theta \sin \phi \hat{\mathbf{y}} + \cos \theta \hat{\mathbf{z}}, \quad (\text{C.7})$$

$$\hat{\boldsymbol{\theta}} = \cos \theta \cos \phi \hat{\mathbf{x}} + \cos \theta \sin \phi \hat{\mathbf{y}} - \sin \theta \hat{\mathbf{z}}, \quad (\text{C.8})$$

$$\hat{\boldsymbol{\phi}} = -\sin \phi \hat{\mathbf{x}} + \cos \phi \hat{\mathbf{y}}. \quad (\text{C.9})$$

C.3 Differential Length, Area, and Volume Elements

In spherical coordinates, the differential displacement vector is

$$d\mathbf{l} = dr \hat{\mathbf{r}} + r d\theta \hat{\boldsymbol{\theta}} + r \sin \theta d\phi \hat{\boldsymbol{\phi}}. \quad (\text{C.10})$$

The corresponding differential area elements are

$$d\mathbf{a}_r = r^2 \sin \theta d\theta d\phi \hat{\mathbf{r}}, \quad (\text{C.11})$$

$$d\mathbf{a}_\theta = r \sin \theta dr d\phi \hat{\boldsymbol{\theta}}, \quad (\text{C.12})$$

$$d\mathbf{a}_\phi = r dr d\theta \hat{\boldsymbol{\phi}}. \quad (\text{C.13})$$

The differential volume element is

$$d\tau = r^2 \sin \theta dr d\theta d\phi. \quad (\text{C.14})$$

C.4 Gradient, Divergence, and Curl in Spherical Coordinates

For a scalar field $\phi(r, \theta, \phi)$, the gradient is

$$\boldsymbol{\nabla} \phi = \hat{\mathbf{r}} \frac{\partial \phi}{\partial r} + \hat{\boldsymbol{\theta}} \frac{1}{r} \frac{\partial \phi}{\partial \theta} + \hat{\boldsymbol{\phi}} \frac{1}{r \sin \theta} \frac{\partial \phi}{\partial \phi}. \quad (\text{C.15})$$

For a vector field $\mathbf{A} = A_r \hat{\mathbf{r}} + A_\theta \hat{\boldsymbol{\theta}} + A_\phi \hat{\boldsymbol{\phi}}$, the divergence is

$$\boldsymbol{\nabla} \cdot \mathbf{A} = \frac{1}{r^2} \frac{\partial}{\partial r} + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} + \frac{1}{r \sin \theta} \frac{\partial A_\phi}{\partial \phi}. \quad (\text{C.16})$$

The curl of \mathbf{A} is given by

$$\boldsymbol{\nabla} \times \mathbf{A} = \frac{1}{r \sin \theta} \begin{vmatrix} \hat{\mathbf{r}} & r \hat{\boldsymbol{\theta}} & r \sin \theta \hat{\boldsymbol{\phi}} \\ \frac{\partial}{\partial r} & \frac{\partial}{\partial \theta} & \frac{\partial}{\partial \phi} \\ A_r & r A_\theta & r \sin \theta A_\phi \end{vmatrix}. \quad (\text{C.17})$$

C.5 Laplacian in Spherical Coordinates

The Laplacian of a scalar field $\phi(r, \theta, \phi)$ in spherical coordinates is

$$\nabla^2 \phi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \phi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \phi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \phi}{\partial \phi^2}. \quad (\text{C.18})$$

Bibliography