

# Lecture Notes on Thermal Physics

Laws of Thermodynamics

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Undergraduate Lecture Notes

Topics Covered:  
Ideal gas • Real gas • 0th Law • 1st Law • problem set

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# Chapter 1

## Terminology

### 1.1 Heat

Heat is defined as the energy in transit between a system and its surroundings solely due to a temperature difference. In thermodynamics, we distinguish between:

- **$Q$  (Finite change):** The total heat exchanged during a process.
- **$\delta Q$  (Infinitesimal change):** A small amount of heat. We use the symbol  $\delta$  instead of  $d$  because heat is a **path function**; its value depends on the process, not just the initial and final states.

#### Sign Convention

- $\delta Q > 0$ : Heat is added to the system.
- $\delta Q < 0$ : Heat is removed from the system.

### 1.2 Heat Capacity

To quantify the relationship between heat added to a system and the resulting change in temperature, we define Heat Capacity. In thermodynamics, it is categorized based on the amount of substance considered.

#### 1.2.1 Specific Heat Capacity( $s$ )

The Specific Heat Capacity ( $s$ ) is the amount of heat required to raise the temperature of unit mass of a substance by 1 K or 1°C.

$$s = \frac{1}{m} \frac{\delta Q}{dT} \quad (\text{SI Unit: } \text{Jkg}^{-1}\text{K}^{-1}) \quad (1.1)$$

It is an intensive property, meaning it does not depend on the total size of the system.

#### 1.2.2 Molar Heat Capacity ( $c$ )

In the study of gases, we often count the number of particles. The **Molar Heat Capacity** ( $c$ ) is the heat required to raise the temperature of **one mole** of the substance by 1 K.

$$c = \frac{1}{n} \frac{\delta Q}{dT} \quad (1.2)$$

- **Unit:**  $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ .
- **intensive property**, meaning it does not depend on the total size of the sample.

#### Problem 1.1. im

Proof that  $c = M s$ : where  $M$  is molar mass of the gas.

### 1.2.3 Heat Capacity ( $C$ )

For our derivations, we focus on the **Total Heat Capacity**. This represents the heat required to raise the temperature of the **entire system** (containing  $n$  moles) by 1 K.

$$C = \frac{\delta Q}{dT} \implies \delta Q = C dT \quad (1.3)$$

- **Unit:**  $\text{J} \cdot \text{K}^{-1}$ .
- It is an **extensive property** and is related to molar capacity by:  $C = nc$ .

#### The Concept of Response Function

In thermodynamics, heat capacity  $C$  acts as the **transfer function** (or response function) that links the **thermal input** ( $\delta Q$ ) to the resulting **thermal response** ( $dT$ ) of the system:

$$\delta Q = C dT$$

## 1.3 State Variables

Properties that describe the condition of a system, such as Pressure ( $P$ ), Volume ( $V$ ), and Temperature ( $T$ ). These are further classified as:

- **Extensive Properties:** Depend on the mass (e.g., Volume, Internal Energy).
- **Intensive Properties:** Independent of the mass (e.g., Temperature, Pressure).

## Chapter 2

# The Zeroth Law of Thermodynamics

### 2.1 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**  $\Theta$ , such that systems in equilibrium are at the same temperature.

### 2.2 Mathematical Formulation

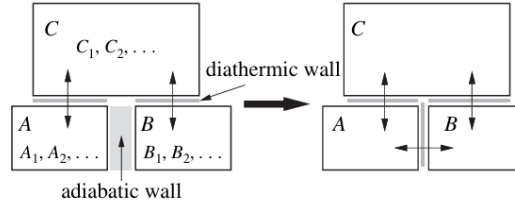


Figure 2.1: 0th Law, thermal Equilibrium

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:

$$f_{AC}(A_1, A_2, \dots; C_1, C_2, \dots) = 0 \quad (2.1)$$

The equilibrium of  $B$  and  $C$  implies a similar constraint:

$$f_{BC}(B_1, B_2, \dots; C_1, C_2, \dots) = 0 \quad (2.2)$$

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

$$C_1 = F_{AC}(A_1, A_2, \dots; C_2, \dots) \quad (2.3)$$

$$C_1 = F_{BC}(B_1, B_2, \dots; C_2, \dots) \quad (2.4)$$

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

$$F_{AC}(A_1, A_2, \dots; C_2, \dots) = F_{BC}(B_1, B_2, \dots; C_2, \dots) \quad (2.5)$$

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:

$$\Theta_A(A_1, A_2, \dots) = \Theta_B(B_1, B_2, \dots) \quad (2.6)$$

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

## 2.3 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  $P$ .

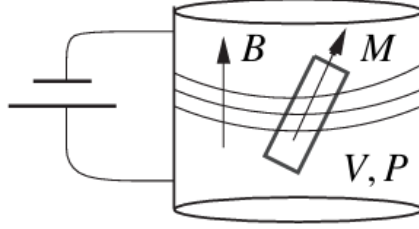


Figure 2.2: paramagnetic van der waals gas

In this system, we observe the following empirical relation similar to 2.6:

$$\frac{1}{N} \left( P + \frac{a}{V^2} \right) (V - b) \propto \frac{NB}{M} \quad (2.7)$$

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

$$\frac{1}{Nk_B} \left( P + \frac{a}{V^2} \right) (V - b) = \frac{N\mu_B^2 B}{3k_B M} = \Theta \quad (2.8)$$

These reproduce two well-known equations of state:

$$\begin{cases} (P + a/V^2)(V - b) = Nk_B T & \text{(van der Waals gas)} \\ M = (N\mu_B^2 B)/(3k_B T) & \text{(Curie paramagnet)} \end{cases} \quad (2.9)$$

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

# Chapter 3

## Ideal Gas

### 3.1 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.

### 3.2 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

$$PV = \text{constant} \quad (3.1)$$

#### 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

$$\frac{V}{T} = \text{constant} \quad (3.2)$$



### 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

$$\frac{P}{T} = \text{constant} \quad (3.3)$$

### 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

$$\frac{V}{n} = \text{constant} \quad (3.4)$$

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).

## 3.3 Ideal Gas Equation

Above mentioned gas laws implies the following proportionality:

$$PV \propto nT \quad (3.5)$$

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

$$\boxed{PV = nRT} \quad (3.6)$$

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:

$$N = nN_A \quad (3.7)$$

Ideal gas equation reduces to:

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

The quantity

$$\frac{R}{N_A} = k_B = 1.380649 \times 10^{-23} \text{ J K}^{-1} \quad (3.8)$$

is defined as the Boltzmann constant.

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

$$\boxed{PV = Nk_B T} \quad (3.9)$$

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

It leads to another form of ideal gas equation:

$$\boxed{P = \bar{n}k_B T} \quad (3.10)$$

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

### 3.4 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:

$$P = \frac{F}{A} \implies F = P \cdot A \quad (3.11)$$

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:

$$\delta W = \vec{F} \cdot d\vec{l} \quad (3.12)$$

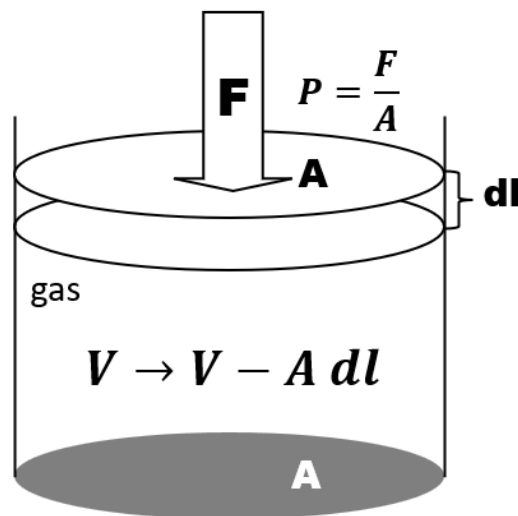


Figure 3.1: Cylinder-piston system: The gas is being compressed by an external force  $F$ .

### 3.4.1 Work Done by the External Agent

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

$$\delta W = (P \cdot A)dl \quad (3.13)$$

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

$$\delta W_{ext} = +P dV \quad (3.14)$$

### 3.4.2 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 ( $dW > 0$ ).

### 3.4.3 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:

$$W = \int_{V_1}^{V_2} P dV \quad (3.15)$$

**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

$$W = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln \left( \frac{V_2}{V_1} \right) \quad (3.16)$$

#### 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

$$W = \int_{V_1}^{V_2} \frac{K}{V^\gamma} dV = \frac{KV_1^{-\gamma}V_1 - KV_2^{-\gamma}V_2}{\gamma - 1} = \frac{P_1V_1 - P_2V_2}{\gamma - 1} \quad (3.17)$$

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

$$W = \int_{V_1}^{V_2} P dV = P(V_2 - V_1) \quad (3.18)$$

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

$$W = nR(T_2 - T_1) \quad (3.19)$$

### 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 3.1

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

## 3.5 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 ( $\Delta p_x$ ) is:

$$\Delta p_x = (-mv_x) - (mv_x) = -2mv_x \quad (3.20)$$

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:

$$f_x = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L} \quad (3.21)$$

### 3.5.1 Pressure

The total force  $F_x$  exerted by all  $N$  molecules is:

$$F_x = \sum_{i=1}^N \frac{mv_{xi}^2}{L} = \frac{m}{L} \sum_{i=1}^N v_{xi}^2 \quad (3.22)$$

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

$$P = \frac{F_x}{L^2} = \frac{m}{L^3} \sum v_{xi}^2 = \frac{m}{V} \sum v_{xi}^2 \quad (3.23)$$

### Root Mean Square Velocity

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

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle \quad (3.24)$$

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

$$P = \frac{1}{3} \frac{Nm \langle v^2 \rangle}{V} \quad (3.25)$$

$$PV = \frac{1}{3}mN\langle v^2 \rangle \quad (3.26)$$

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

$$P = \frac{1}{3}\rho v_{rms}^2 \quad (3.27)$$

### 3.5.2 Kinetic Energy and Temperature

From the ideal gas law  $PV = Nk_B T$  and 3.26:

$$\frac{1}{3}Nm v_{rms}^2 = Nk_B T \quad (3.28)$$

The average translational kinetic energy of a single molecule is:

$$\kappa_{avg} = \langle \frac{1}{2}mv^2 \rangle = \frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}m v_{rms}^2 = \frac{3}{2}k_B T \quad (3.29)$$

#### Key Insight

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

## 3.6 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  $\frac{1}{2}k_B T$ .

### 3.6.1 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:

$$\bar{\kappa} = \frac{3}{2}k_B T \quad (3.30)$$

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 ( $x, y, z$ ).

### 3.6.2 Analysis of Degrees of Freedom ( $f$ )

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

$$u_{av} = 3 \times \left( \frac{1}{2} k_B T \right) = \frac{3}{2} k_B T \quad (3.31)$$

- **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  $f = 5$ .

$$u_{av} = 5 \times \left( \frac{1}{2} k_B T \right) = \frac{5}{2} k_B T \quad (3.32)$$

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

## 3.7 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.

In simple language: if we randomly choose a molecule in a gas and look at its velocity, the probability of finding its velocity in the infinitesimal volume  $d^3v$  (centered at  $\vec{v} = v_x, v_y, v_z$ ) is given by  $f(\vec{v})d^3v$ .

Similarly, If we ask the question of what is the probability of finding only the  $x$ -component of the velocity to be  $v_x$  within a range  $dv_x$ , that probability will be  $f(v_x)dv_x$ .

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

$$f(\vec{v})d^3v = f(v_x)f(v_y)f(v_z)dv_xdv_ydv_z \quad (3.33)$$

#### 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  $\epsilon_i$  is proportional to the Boltzmann factor:

$$n_i \propto e^{-\frac{\epsilon_i}{k_B T}} \quad (3.34)$$

$$n_i = \frac{N}{Z} e^{-\frac{\epsilon_i}{k_B T}} \quad (3.35)$$

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:

$$\frac{N_\epsilon d\epsilon}{N} = f(\epsilon)d\epsilon = A e^{-\frac{\epsilon}{k_B T}} d\epsilon \quad (3.36)$$

where  $A$  is a normalization constant.

Based on the Boltzmann factor  $e^{-\epsilon/k_B T}$ , where  $E = \frac{1}{2}mv^2$ , the distribution for a single component is:

$$f(v_x)dv_x = A \exp\left(-\frac{mv_x^2}{2k_B T}\right) dv_x \quad (3.37)$$

#### Normalization Constant

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

$$\int_{-\infty}^{\infty} f(v_x) dv_x = 1. \quad (3.38)$$

Substituting the expression for  $f(v_x)$ ,

$$A \int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2k_B T}} dv_x = 1. \quad (3.39)$$

Using the standard Gaussian integral

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}, \quad (3.40)$$

we obtain

$$\int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2k_B T}} dv_x = \sqrt{\frac{2\pi k_B T}{m}}. \quad (3.41)$$

which yields

$$A = \sqrt{\frac{m}{2\pi k_B T}}. \quad (3.42)$$



### 3.7.1 Velocity distribution

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

$$f(v_x)dv_x = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{mv_x^2}{2k_B T}\right) dv_x \quad (3.43)$$

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

$$f(v_x, v_y, v_z)d^3v = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T}\right) dv_x dv_y dv_z \quad (3.44)$$

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:

$$f(\vec{v})d^3\vec{v} = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right) d^3\vec{v} \quad (3.45)$$

To find the Speed Distribution, we look at the magnitude  $v$ . We integrate over all possible directions in velocity space (spherical coordinates), where the volume element  $d^3v$  becomes  $4\pi v^2 dv$ :

$$F(v)dv = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) dv \quad (3.46)$$

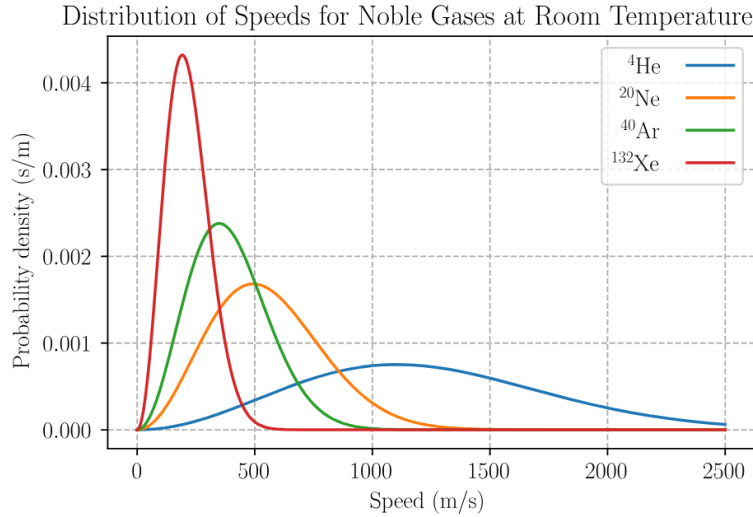


Figure 3.2: Velocity distributions of inert gases

#### Most Probable Speed ( $v_{mp}$ )

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

$$\frac{d}{dv} \left[ v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) \right] = 0 \quad (3.47)$$

yields:

$$\boxed{v_{mp} = \sqrt{\frac{2k_B T}{m}}} \quad (3.48)$$

### Average Speed ( $v_{avg}$ )

The average is the first moment of the distribution:

$$\langle v \rangle = \int_0^\infty v F(v) dv = \sqrt{\frac{8k_B T}{\pi m}} \quad (3.49)$$

$$\boxed{\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}} \quad (3.50)$$

### Root Mean Square Speed ( $v_{rms}$ )

The mean square speed is the second moment:

$$\langle v^2 \rangle = \int_0^\infty v^2 F(v) dv = \frac{3k_B T}{m} \quad (3.51)$$

$$\boxed{v_{rms} = \sqrt{\frac{3k_B T}{m}}} \quad (3.52)$$

The relationship between these speeds is:

$$\boxed{v_{mp} < v_{avg} < v_{rms}} \quad (3.53)$$

## 3.7.2 Momentum

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

$$F(p) dp = 4\pi \left( \frac{1}{2\pi m k_B T} \right)^{3/2} p^2 \exp \left( -\frac{p^2}{2m k_B T} \right) dp \quad (3.54)$$

## 3.7.3 Energy Distribution

The kinetic energy of a gas molecule is given by

$$\epsilon = \frac{1}{2} m v^2. \quad (3.55)$$

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

$$F(\epsilon) d\epsilon = \frac{2}{\sqrt{\pi}} \frac{1}{(kT)^{3/2}} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon. \quad (3.56)$$

### Averag energy

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

$$\langle \epsilon \rangle = \frac{3}{2}kT. \quad (3.57)$$

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

$$F(\epsilon)d\epsilon = \frac{2\sqrt{\epsilon}}{\sqrt{\pi}(k_B T)^{3/2}} \exp\left(-\frac{\epsilon}{k_B T}\right) d\epsilon \quad (3.58)$$

## 3.8 Transport phenomenon

### 3.8.1 Mean free path

The *mean free path* ( $\lambda$ ) is defined as the average distance traveled by a gas molecule between two successive collisions. To derive this, we model gas molecules as hard spheres of diameter  $d$ .

#### Collision Rate

Consider a single molecule 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:

$$dV = \sigma v dt = \pi d^2 v dt \quad (3.59)$$

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:

$$dN = n(\pi d^2 v dt) \quad (3.60)$$

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

$$f = \frac{dN}{dt} = n\pi d^2 v \quad (3.61)$$

#### Mean Free Path

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

$$\tau = \frac{1}{n\pi d^2 v} \quad (3.62)$$

The mean free path  $\lambda$  is the distance covered during this time:

$$\lambda = v\tau = \frac{1}{n\pi d^2} \quad (3.63)$$

### Correction for Relative Motion

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:

$$v_{rel}^2 = v_1^2 + v_2^2 - 2\vec{v}_1 \cdot \vec{v}_2 \quad (3.64)$$

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:

$$\lambda = \frac{1}{\sqrt{2}n\pi d^2} \quad (3.65)$$

### Dependence on Temperature and Pressure

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

$$\lambda = \frac{k_B T}{\sqrt{2}\pi d^2 P} \quad (3.66)$$

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

#### 💡 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 ( $\lambda$ ).

Table 3.1: Primary Transport Phenomena

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

### 3.8.2 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:

$$p_{\downarrow} = \frac{1}{6}nm\bar{v} \left( u + \lambda \frac{du}{dz} \right) \quad (3.67)$$

The upward momentum flux  $p_{\uparrow}$  is:

$$p_{\uparrow} = \frac{1}{6}nm\bar{v} \left( u - \lambda \frac{du}{dz} \right) \quad (3.68)$$

The net momentum transfer per unit area per unit time (shear stress  $\tau$ ) is the difference:

$$\tau = p_{\downarrow} - p_{\uparrow} = \frac{1}{6}nm\bar{v} \left( 2\lambda \frac{du}{dz} \right) = \frac{1}{3}nm\bar{v}\lambda \frac{du}{dz} \quad (3.69)$$

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

$$\boxed{\eta = \frac{1}{3}nm\bar{v}\lambda} \quad (3.70)$$

#### Properties of Gas Viscosity

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

### 3.8.3 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  $\epsilon$  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  $q$ :

$$q = \frac{1}{6}n\bar{v} \left( \epsilon - \lambda \frac{d\epsilon}{dz} \right) - \frac{1}{6}n\bar{v} \left( \epsilon + \lambda \frac{d\epsilon}{dz} \right) \quad (3.71)$$

$$q = -\frac{1}{3}n\bar{v}\lambda\frac{d\epsilon}{dz} \quad (3.72)$$

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

$$q = -\left(\frac{1}{3}n\bar{v}\lambda C_v\right) \frac{dT}{dz} \quad (3.73)$$

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

$$\boxed{K = \frac{1}{3}n\bar{v}\lambda C_v} \quad (3.74)$$

### properties of Thermal conductivity

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

$$\frac{K}{\eta} = \frac{C_v}{m} = s_v \quad (3.75)$$

$$\boxed{K = \eta m C_v} \quad (3.76)$$

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

### 3.8.4 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  $(n + \lambda \frac{dn}{dz})$ :

$$J = \frac{1}{6}\bar{v} \left( n - \lambda \frac{dn}{dz} \right) - \frac{1}{6}\bar{v} \left( n + \lambda \frac{dn}{dz} \right) \quad (3.77)$$

$$J = -\frac{1}{3}\bar{v}\lambda \frac{dn}{dz} \quad (3.78)$$

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

$$\boxed{D = \frac{1}{3}\bar{v}\lambda} \quad (3.79)$$

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

# Chapter 4

## First Law of Thermodynamics

### 4.1 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:

$$U = \sum_{i=1}^N \left( \frac{1}{2}mv_i^2 + \frac{1}{2}I\omega_i^2 + E_{vib,i} \right) + U_{potential} + \dots \quad (4.1)$$

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.

### 4.1.1 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**:

$$U = U(T) \quad (4.2)$$

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.

## 4.2 The First Law of Thermodynamics

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

The heat  $\delta Q$  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

$$Q = \Delta U + W \quad (4.3)$$

where  $W$  is the work done by the system.

In differential form,

$$\delta Q = dU + \delta W \quad (4.4)$$

or, equivalently, the more convenient form,

$$dU = \delta Q - \delta W \quad (4.5)$$

### 4.2.1 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

$$\delta W = P dV \quad (4.6)$$

Hence, the First Law becomes

$$dU = \delta Q - P dV \quad (4.7)$$



### 4.2.2 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

$$\delta W' = \sum_i J_i dX_i \quad (4.8)$$

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 $\gamma$	Area $dA$	$\gamma dA$
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

$$\delta Q + \delta W' = dU + \delta W \quad (4.9)$$

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

$$dU = \delta Q - P dV + \sum_i J_i dX_i \quad (4.10)$$

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

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

$$\boxed{dU = \delta Q + \sum_i J_i dX_i} \quad (4.11)$$

### 4.2.3 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  $\mu_i$  is the corresponding chemical potential, then the chemical work term is

$$\delta W_{\text{chem}} = - \sum_i \mu_i dN_i \quad (4.12)$$

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

$$\boxed{dU = \delta Q + \sum_i J_i dX_i + \sum_i \mu_i dN_i} \quad (4.13)$$

## 4.3 Applications of the First Law of Thermodynamics

### 4.3.1 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

$$C = \frac{\delta Q}{dT} \quad \implies \quad \delta Q = C dT \quad (4.14)$$

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

$$\delta W = P dV = 0 \quad (4.15)$$

According to the First Law of Thermodynamics,

$$dU = \delta Q_V \quad (4.16)$$

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

$$\boxed{dU = C_V dT} \quad (4.17)$$

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,

$$\delta Q_P = dU + P dV \quad (4.18)$$

By definition,

$$\delta Q_P = C_P dT \quad (4.19)$$

Therefore,

$$C_P = \left( \frac{\delta Q}{dT} \right)_P = \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P \quad (4.20)$$

Using the definition of  $C_V$ , this may be written as

$$\boxed{C_P = C_V + P \left( \frac{\partial V}{\partial T} \right)_P} \quad (4.21)$$

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,

$$C_P > C_V \quad (4.22)$$

#### Mayer's Relation for an Ideal Gas ( $n$ moles)

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

$$\left( \frac{\partial V}{\partial T} \right)_P = \frac{nR}{P} \quad (4.23)$$

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

$$\boxed{C_P - C_V = nR} \quad (4.24)$$

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

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

$$\delta Q = 0 \quad (4.25)$$

The First Law of Thermodynamics,

$$dU = \delta Q - P dV, \quad (4.26)$$

therefore reduces to

$$dU = -P dV. \quad (4.27)$$

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

$$dU = C_V dT. \quad (4.28)$$

Hence,

$$C_V dT = -P dV. \quad (4.29)$$

The equation of state of an ideal gas is

$$PV = nRT, \quad (4.30)$$

which implies

$$P dV + V dP = nR dT. \quad (4.31)$$

**Using the definition of heat capacities:**

At constant pressure,

$$\delta Q_P = C_P dT = dU + P dV, \quad (4.32)$$

which gives

$$C_P = C_V + P \left( \frac{\partial V}{\partial T} \right)_P. \quad (4.33)$$

For an ideal gas,

$$\left( \frac{\partial V}{\partial T} \right)_P = \frac{nR}{P}, \quad (4.34)$$

and therefore Mayer's relation follows:

$$C_P - C_V = nR. \quad (4.35)$$

**Combining Eqs. (4.29) and (4.31):**

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

$$\frac{dP}{P} + \gamma \frac{dV}{V} = 0. \quad (4.36)$$

Integrating,

$$\boxed{PV^\gamma = \text{constant}}. \quad (4.37)$$

### Example: Adiabatic Condition for a Van der Waals Gas

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

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT, \quad (4.38)$$

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,

$$\delta Q = 0, \quad (4.39)$$

and hence, from the first law of thermodynamics,

$$dU = \delta W. \quad (4.40)$$

For a reversible process, the work done is

$$\delta W = -P dV. \quad (4.41)$$

### Internal Energy of a Van der Waals Gas

The differential form of internal energy for a real gas is

$$dU = C_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV. \quad (4.42)$$

For a Van der Waals gas,

$$\left( \frac{\partial U}{\partial V} \right)_T = \frac{a}{V^2}, \quad (4.43)$$

which represents the contribution of intermolecular forces.

Thus,

$$dU = C_V dT + \frac{a}{V^2} dV. \quad (4.44)$$

### Adiabatic Condition

Using  $dU = -P dV$ , we obtain

$$C_V dT + \frac{a}{V^2} dV + P dV = 0. \quad (4.45)$$

Substituting the Van der Waals equation for  $P$ ,

$$P = \frac{RT}{V-b} - \frac{a}{V^2}, \quad (4.46)$$

the equation becomes

$$C_V dT + \frac{RT}{V-b} dV = 0. \quad (4.47)$$

### Integration

Rearranging,

$$\frac{dT}{T} = -\frac{R}{C_V} \frac{dV}{V-b}. \quad (4.48)$$

Integrating,

$$\ln T = -\frac{R}{C_V} \ln(V-b) + \text{constant}. \quad (4.49)$$

Hence,

$$T(V-b)^{\frac{R}{C_V}} = \text{constant}. \quad (4.50)$$

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

$$\boxed{\left( P + \frac{a}{V^2} \right) (V-b)^{1+(R/C_V)} = \text{constant}.} \quad (4.51)$$

### 4.3.3 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:

$$E = \frac{\text{stress}}{\text{strain}} = -V \left( \frac{\partial P}{\partial V} \right). \quad (4.52)$$

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

**Isothermal Elasticity**

For an isothermal process,

$$PV = \text{constant}. \quad (4.53)$$

Differentiating,

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{P}{V}. \quad (4.54)$$

Hence, the isothermal elastic modulus is

$$E_T = -V \left(\frac{\partial P}{\partial V}\right)_T = PV. \quad (4.55)$$

**Adiabatic Elasticity**

For an adiabatic process,

$$PV^\gamma = \text{constant}, \quad (4.56)$$

where  $\gamma = C_P/C_V$ .

Differentiating,

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

Thus, the adiabatic elastic modulus becomes

$$E_S = -V \left(\frac{\partial P}{\partial V}\right)_S = \gamma PV. \quad (4.58)$$

**Ratio of Elasticities**

The ratio of adiabatic to isothermal elasticity is therefore

$$\boxed{\frac{E_S}{E_T} = \gamma = \frac{C_P}{C_V}} \quad (4.59)$$

## 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.

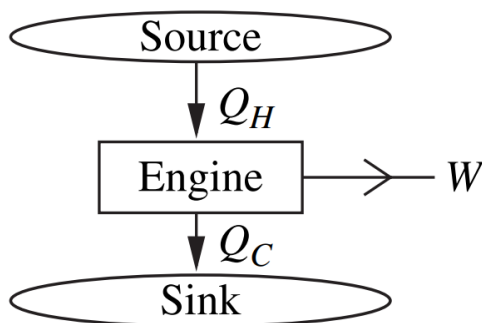


Figure 5.1: Heat Engine

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:

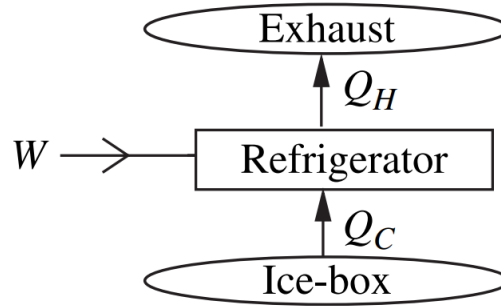


Figure 5.2: Refrigerator

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

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

#### 5.3.1 Kelvin's statement

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

#### 5.3.2 Clausius's statement

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

#### 5.3.3 Equivalence of both statements

##### 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 boy 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  $W$ .



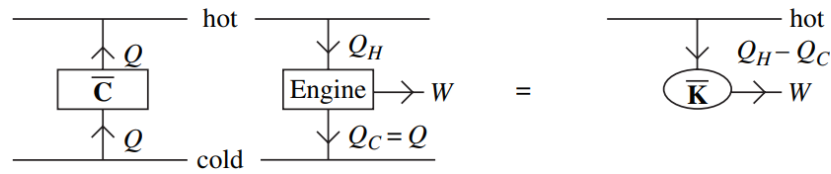


Figure 5.3: Anti-clausius Engine is equivalent to Anti-Kelvin Engine

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

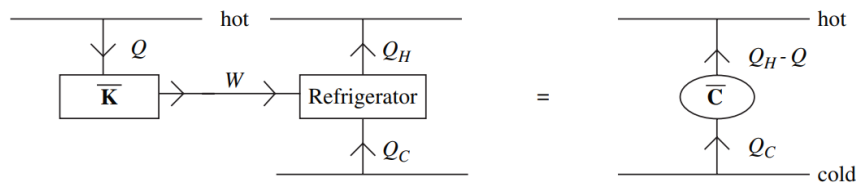


Figure 5.4: Anti-Kelvin Engine is equivalent to Anti-clausius Engine

Lets consider an anti-kelvin engine, that takes  $Q$  heat from a hot body and completely 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.

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

we basically shown that violation of one statement is equivalent to violating 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

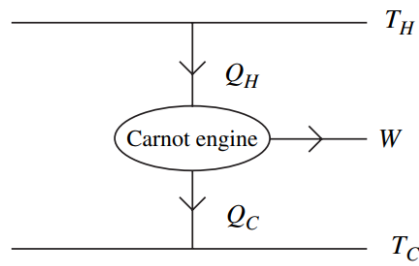


Figure 5.5: Carnot Engine

### 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.

# Chapter 6

## Thermodynamic potentials

### 6.1 Internal Energy U

As already introduced in chapter 4, Internal energy is the total energy of the system.

By First Law of thermodynamics:

$$dU = TdS + J \cdot dx + \mu \cdot dN \quad (6.1)$$

also implies

$$\left. \frac{\partial U}{\partial S} \right|_{x,N} = T \quad \left. \frac{\partial U}{\partial x} \right|_{S,N} = J \quad \left. \frac{\partial U}{\partial N} \right|_{x,S} = \mu \quad (6.2)$$

For fixed Intensive coordinates  $(T, J, \mu)$ , the extensive quantities are simply proporsional to system's size.

#### 6.1.1 Gibbs-Dulhem relation

Let say system is Enlarged by factor  $\lambda$ , than absolute internal energy  $U(S, x, N)$  will be:

$$U(\lambda S, \lambda x, \lambda N) = \lambda U(S, x, N) \quad (6.3)$$

Lets differertiate it, with respect to  $\lambda$ ,

$$\frac{\partial U}{\partial(\lambda S)} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda x)} \frac{\partial(\lambda x)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda N)} \frac{\partial(\lambda N)}{\partial \lambda} = U(S, x, N) \quad (6.4)$$

simplifing and putting  $\lambda = 1$ ,

$$\boxed{U = TS + J \cdot x + \mu \cdot N} \quad (6.5)$$

It shows that, U contains Thermal energy  $TS$ , Chemical Potential Energy  $\mu \cdot N$ , system being worked  $J \cdot x$ .

6.5, implies

$$dU = TdS + SdT + J \cdot dx + x \cdot dJ + \mu \cdot dN + N \cdot d\mu \quad (6.6)$$

By 6.1 and 6.6, We conclude:

$$\boxed{SdT + x \cdot dJ + N \cdot d\mu = 0} \quad (6.7)$$

It is known as Gibbs-duhem relation or Fundamental Equation of thermodynamics.

### 6.1.2 First Maxwells relation

The systems we are interested in, are having four parameters T, V, P, S.  
hence First law of thermodynamics implies:

$$\boxed{dU = TdS - PdV} \quad (6.8)$$

this implies

$$\frac{\partial^2 U}{\partial S \partial V} = \boxed{\frac{\partial T}{\partial V} = -\frac{\partial P}{\partial S}} \quad (6.9)$$

## 6.2 Enthalpy H

**For an adiabatically isolated system, Entropy must increase in any spontaneous change and reaches a maximum in equilibrium.**

But what about systems, that are subjected to external mechanical work  $J \cdot dx$  ( $PdV$  for example).

Enthalpy is the appropriate function when there is no heat exchange ( $\delta Q = 0$ ), minimum Enthalpy principle determines systems equilibrium state.

$$H = U - J \cdot x \quad (6.10)$$

for the systems we are interested in (P, V, T, S)

$$\boxed{H = U + PV} \quad (6.11)$$

### 6.2.1 Second Maxwell relation

This implies

$$dH = dU + PdV + VdP \quad (6.12)$$

from Eq. 6.8

$$\boxed{dH = TdS + VdP} \quad (6.13)$$

## 6.3 Helmholtz Free Energy F

$$\boxed{F = U - TS} \quad (6.14)$$

This implies,

$$dF = dU - TdS - SdT \quad (6.15)$$

$$\boxed{dF = -PdV - SdT} \quad (6.16)$$

## 6.4 Gibbs Free Energy G

# Appendix A

## Equation of states

### A.1 Berthelot Equation of State

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

**Parameters:**

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

### A.2 Clausius Equation of State

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

**Parameters:**

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

### A.3 Virial Equation of State

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

**Parameters:**

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

## A.4 Redlich–Kwong Equation of State

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

**Parameters:**

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

## A.5 Soave–Redlich–Kwong (SRK) Equation

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

**Parameters:**

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

## A.6 Peng–Robinson Equation of State

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

**Parameters:**

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

## A.7 Hard-Sphere Equation of State

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

**Parameters:**

- $Z$  : compressibility factor
- $\eta$  : packing fraction

## A.8 Benedict–Webb–Rubin (BWR) Equation

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

**Parameters:**

- $A_0, B_0, a, b, \alpha$  : empirical constants obtained from experiment

## A.9 Degenerate Fermi Gas Equation of State

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

**Parameters:**

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

## A.10 Bose Gas Equation of State

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

**Parameters:**

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

## A.11 Radiation Equation of State

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

**Parameters:**

- $a$  : radiation constant

# Bibliography