

THERMODYNAMICS

$$dU = Tds - PdV + \mu dN$$

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CHAPTER 1: Introduction

Objectives

This chapter aims to:

- *To make the students familiar with the basic thermodynamics concepts such as system, surrounding, Boundary, Universe, state, thermodynamic path, process, thermal equilibrium, and Temperature.*
- *Review the concept of triple point, temperature scales.*
- *To introduce the students with temperature measurements instruments.*

1. **Thermodynamics:** It's concerned with *Thermal energy (often called internal energy)* and its applications. It's a **phenomenological theory** of the **macroscopic** properties of **system** at certain **equilibrium state**. This theory describes the system in terms of a few experimentally measurable parameters like - *Volume, Pressure P, Temperature T, Density ρ , ...etc.*

The laws of thermodynamics are general and primitive (axioms). These laws cannot be derived from anything more basic).

2. **Thermodynamic system/ System:** It is any quantity of matter, any region of space, selected for study, see figure 1.

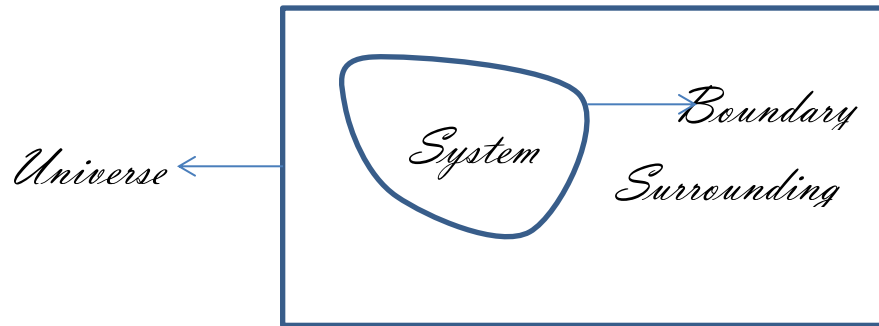
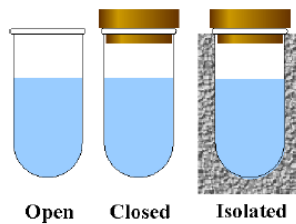


Figure 1

3. **Surrounding:** everything outside the system is called surrounding
4. **Boundary :** The envelope (imaginary or real) which encloses a system and separates it from its surrounding.
5. **Universe:** System and surrounding together are called universe (System+ Surrounding = Universe).
6. **Types of system: There are three types of system:**
 - (I) **Open system:** The boundary of this system permits either matter or energy or both to be exchange with its surrounding. (ex.: boiling of water in an open vessel).
 - (II) **Closed system:** the boundary of this system permits only energy to be exchange with the surrounding. (ex. : boiling of water in a closed vessel)
 - (III) **Isolated system:** An isolated system can exchange neither energy nor matter with the surrounding. (ex.: system and its surrounding is an example of isolated system).



(Phenomenological theory means that it does not provide **the microscopic** origin of a phenomenon)

7. Thermodynamic quantities (thermodynamics coordinates, or thermodynamic variables):

There are certain characteristics by which the physical condition of a system may be described, e.g. *Volume V, Pressure P, Temperature T*. such properties is known as the properties of a system. When all the properties of the system are known the system is said to have a definite state. These properties are called the *thermodynamic coordinates* of the system

8. Types of quantities:

Classified as either extensive or intensive¹

(I) **Extensive quantities** : quantities proportional to the amount of matter present. Suppose we have a system and we double it. That means that we double the volume V , double the number of particles N , double the internal energy U , and double the entropy S . Quantities such as V , N , U , and S which are **additive** are called extensive.

(I) **Intensive quantities**: quantities independent of the amount of matter present. The variables which arise from differentiating the entropy, such as temperature $1/T = \partial S/\partial E$ and pressure $p = T \partial S/\partial V$ and chemical potential $\mu = T\partial S/\partial N$ involve the ratio of two extensive quantities and so do not change as we scale the system: they are called intensive quantities.

“An easy way to determine whether a property is intensive or extensive is to divide the system into two equal parts with an imaginary partition, as shown in Fig. 2–6. Each part will have the same value of intensive properties as the original system, but half the value of the extensive properties [1]”

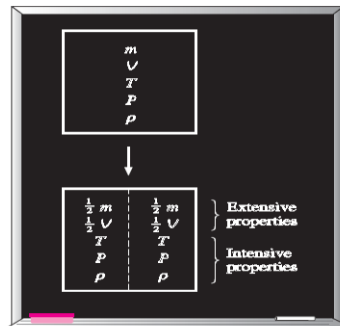


FIGURE 2-6
Criteria to differentiate intensive and extensive properties.

11. State: The word state represent all the macroscopic properties (variables) associated with a system.

¹ Kant formulate his distinction between extensive and intensive magnitudes. According to Kant, extensive magnitudes are those “in which the representation of the parts makes possible the representation of the whole”

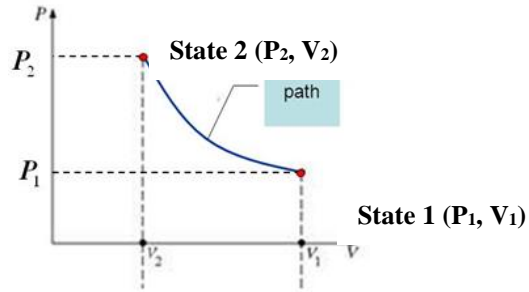


Figure 2

- 12. **Path:** The successive states passes through during process is called the path.
- 13. **Process:** Transformation from one equilibrium state to another

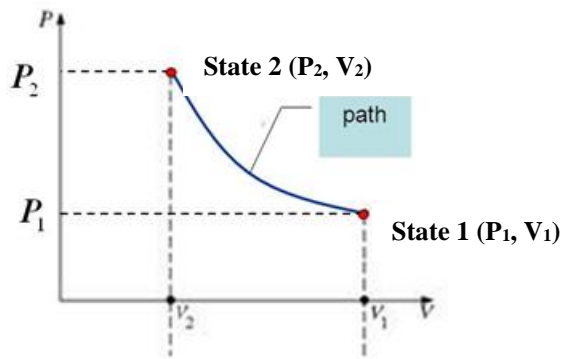


Figure 3: Process 1 → 2

- 14. **Cycle :** if the system go back to its initial after a series of states, this process is called cycle, or thermodynamic cycle.

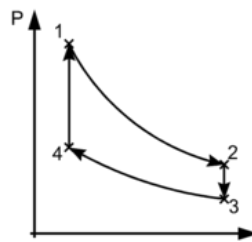
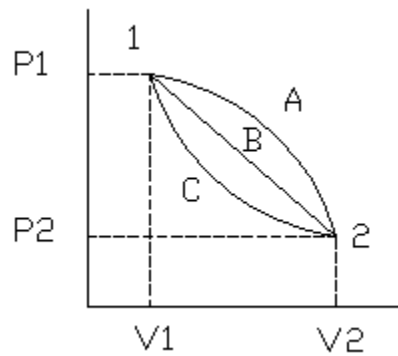


Figure 4: Example of thermodynamic cycle.

Q: Find out the state, properties, path, process, and cycle from the figure below given below.



Ans. States: State 1 and State 2

Properties: Pressure (P), and Volume (V)

Paths: path A, Path B, and Path C

Process : Process 1 \longrightarrow 2 , or process 2 \longrightarrow 1

Cycle: 1 \longrightarrow 2 \longrightarrow 1

Classification of thermodynamic processes :

- I. **Quasi-static process:** the transformation proceeds *sufficiently slowly* (a mathematically infinitesimal paths) so that the system can be considered to remain in equilibrium at the average of the two point in the path.
- II. **Reversible process:** quasi-static transformation is usually reversible, that is, the system will traces the transformation in reverse, when the external change is reversed. A reversible transformation can be represented by a continuous path, as illustrated in Fig.5.

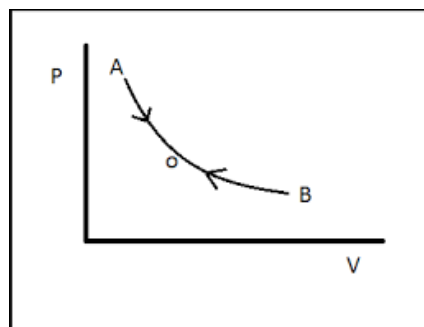
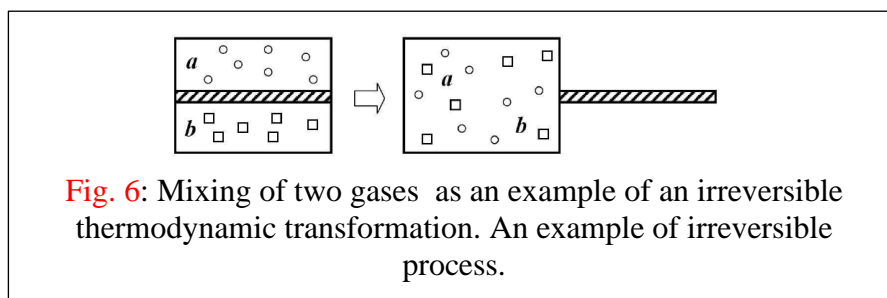


Figure 5 (Quasi-static process is reversible process)

- III. **Irreversible process:** an irreversible transformation cannot be retraced by reversing the external conditions. Such a transformation cannot be represented by a path in the equation-of-state space. Figure 6 is an example of an irreversible transformation is mixing of two gases by removing the separation wall



The following table shows a comparison between reversible and irreversible process:

Reversible Process	Irreversible Process
1. The process is carried out infinitesimally slowly	1. It is carried out rapidly
2. At any stage, the equilibrium is not disturbed	2. Equilibrium may exist only after the completion of the process.
3. It takes infinite time for completion.	3. It takes a finite time for completion.
4. Work obtained in this process is maximum.	4. Work obtained in this process is not maximum

9. Thermal equilibrium, the zeroth Law of thermodynamic, and temperature

10.1 Thermal equilibrium

If two thermodynamic systems such as gases are put in thermal contact, after a time no further changes in the pressure and volumes will occur, and the gasses are said to be in *thermal equilibrium* with each other. Generally, *thermal equilibrium is the state achieved by two (or more) systems, characterized by restricted values of the coordinates of the system, after they have been in communication with each other through diathermal wall.*

10.2 Zeroth law of thermodynamics

If each of two systems is in thermal equilibrium with a third, then they are also in thermal equilibrium with each other.

This implies the existence of a property called *temperature*. Two systems that are in thermal equilibrium with each other must have the same temperature.

10.3 Temperature:

“ The temperature of a system is a property that determines whether or not that system in thermal equilibrium with other systems”.

Measuring Temperature:

Any thermoscope (device that measures temperature) must satisfy the following properties:

- I. It should be based on an easily measured macroscopic quantity such as volume, resistance, etc.
- II. The function that relates the chosen parameter with temperature, $T = f(a)$, should be monotonic.
- III. The quantity should be measurable over as wide a range of T as possible.

First define and measure temperatures on the Kelvin scale. Then we calibrate a thermoscope so as to make it a thermometer.

➤ **The absolute (Kelvin) temperature scale:**

This scale is based on *the triple point of water* ($T = 273.16 \text{ K}$ and $P = 611.73 \text{ Pa}$) where water can coexist in the solid, liquid, and gas phases in equilibrium). This new *absolute temperature scale* (also called the *Kelvin scale*). This scale use the kelvin to be the SI unit of absolute temperature.

Kelvin : is $1/273.16$ of the difference between absolute zero and the temperature of the triple point of

➤ **Note that** we do not use a degree mark in reporting Kelvin temperatures It is 300 K (not 300°K), and it is read "300 kelvins" (not "300 degrees Kelvin").

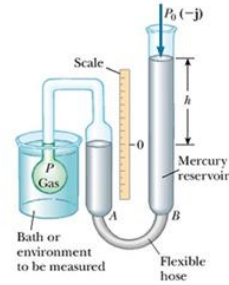


Figure 7(a)

➤ **The constant –volume gas thermometer**

It is the standard thermometer, against which all other thermometers are calibrated. It is based on measuring the pressure of a gas in *a fixed volume*. it consists of a gas-filled bulb connected by a tube to a mercury manometer. By *raising* and *lowering* reservoir R, the mercury level in the left arm of the U-tube can always be brought to the zero of the scale to keep the gas volume constant. The temperature of the path or any body in thermal contact with the bulb is (according to the ideal gas law, where the volume is constant):

$$T = CP \quad (1.1)$$

In which P is the pressure of the gas, and C is constant. The pressure P is given as;

$$P = P_0 \pm \rho gh \dots (1.2)$$

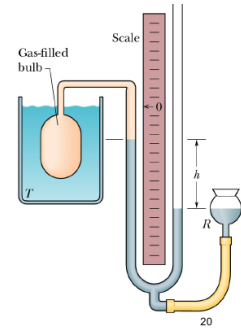


Figure 7(b)

Where P_0 is the atmospheric pressure, ρ is the density of mercury, and h is the measured difference between the mercury levels in the two arms of the tube (The sign is positive if P is measured down the level at which the pressure is P_0 , and vice versa, Figure 7 (a,b)).

If we next put the bulb in a triple-point cell (Fig. 8), the temperature now being measured is:

$$T_3 = CP_3 \dots (1.3)$$

P_3 is the gas pressure now. Eliminating C between eqs. And gives us the temperature as

$$T = T_3 \left(\frac{P}{P_3} \right) = (273.16\text{K}) \left(\frac{P}{P_3} \right) \dots (1.4)$$

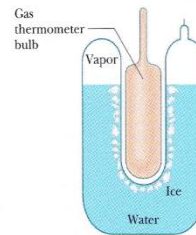


Fig. 8

Consider measuring the *ideal –gas temperature* at the normal boiling point of water (the steam point). An amount of gas is introduced into the bulb of a constant –volume gas thermometer, and one measure P_3

when the bulb of the constant –volume gas thermometer is inserted in the triple point cell shown in Fig. 8. Suppose that $P_3 = 120\text{kPa}$ Keeping the volume V constant, carry out the following procedures:

- I) Surround the bulb with steam at standard atmospheric pressure, measure the gas pressure P , and calculate the empirical T using eq. (1.4) ,

$$T = (273.16\text{K}) \left(\frac{P}{120} \right)$$

- II) Then repeat both measurements with a smaller amount of gas in the bulb. So that P_3 has a smaller value, say, 60kPa . Measure the new value of P and calculate a new value,

$$T = (273.16\text{K}) \left(\frac{P}{60} \right)$$

- III) Continue reducing the amount of gas in the bulb so that P_3 and P have smaller and smaller values, P_3 having values of say, 40kPa , 20kPa , etc. At each value of P_3 and P calculate the corresponding T .

- IV) Plot T against P_3 and extrapolate the resulting curve to the axis where $P_3 = 0$. Read T from the graph, Fig. (9).

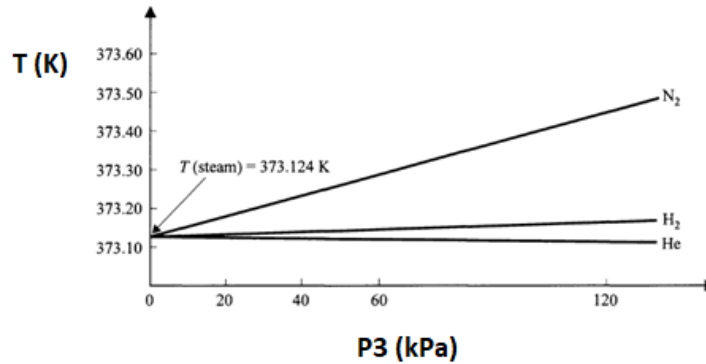


Figure (9) shows $T(\text{K})$ versus P_3 (kPa) for three different gases in order to measure the temperature of boiling water. It is clear that, although the readings of a constant –volume gas thermometer depend upon the nature of the gas, *all gases indicate the same temperature as P_3 is lowered and made approach zero.*

Therefore ,generally, we define *the ideal gas temperature* as:

$$T = 273.16 \text{ K} \lim_{P_3 \rightarrow 0} \left(\frac{P}{P_3} \right) \cdots \cdots (\text{constant } V) \cdots \cdots (1.5)$$

11.1 The Celsius Scale

- The Celsius temperature scale, named after the Swedish astronomer Anders Celsius.
- The Celsius scale (formerly called the centigrade scale).
- The Celsius temperature are measured in degrees, and the Celsius degree has the same size as the kelvin. However, the zero of the Celsius scale is shifted to the ice point of water 273.15 K.
- If T_C represents a Celsius temperature and T a Kelvin temperature, then;

$$T_C = T - 273.15 \dots \dots (1.5)$$

➤ Platinum Resistance thermometers

Resistance thermometer is based on the variation of electrical resistance of a metal with temperature, cover an even greater range. Platinum is of a metal with temperature, cover an even greater range. Platinum is Often because:

- I) It is comparatively easy to purify, purity improving its performance at low temperatures.
- II) It also has a high melting point (1770 °C). Between 70 K and 1200 °C it is capable of very high accuracy, It is not far from linear.

For a moderate accuracy, the instrument calibrate to a quadratic relation between the resistance and temperature;

$$R(T) = R'_T(1 + aT + bT^2) \dots \dots (1.6)$$

$R(T)$: Is the resistance of platinum at temperature T .

R'_T : Is the resistance of platinum when it is surrounded by a water at triple point.

a , and b are constants.

➤ Radiation thermometry

None of the thermometers described above is useful far above the gold point (1064 °C) and in this range radiation pyrometers are used. ***These are based on measurement of the radiation emitted by a body when hot.*** In radiation thermometry we use the Planck radiation law, which relates thermodynamic temperature to the measured spectral radiance.

➤ Thermocouples

Schematic diagram of thermocouple is shown in Figure (10). Thermocouples, thermometers using the variation of the Seebeck e.m.f. with temperature range. Where the temperature to be measured is located at the test junction. Thermal electromotive force is generated at the junction of the two point A and B . The

two thermocouple wire are connected to copper wires located the reference junction which is maintained at the melting point of ice. junction . The e.m.f. is generally well represented by an expression of the form

$$\varepsilon = c_0 + c_1T + c_2T^2 + c_3T^3 \quad (1.7)$$

Where ε is the thermal emf and c_0, c_1, c_2, c_3 are constants depend on the thermocouple.

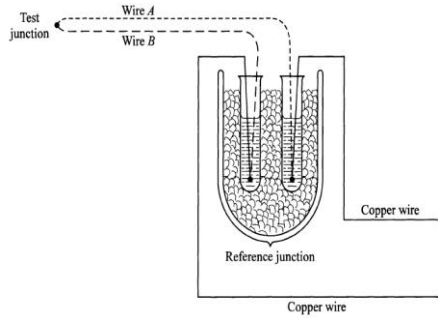


Figure 610

Table 1 : Some Common thermocouples.

Pair	Approximate sensitivity/ $\mu\text{V K}^{-1}$	Normal working range/ $^{\circ}\text{C}$
copper–constantan ^a	40	–200 to +300
iron–constantan	50	–200 to +750
chromel ^b –alumel ^c	40	–200 to +1200
platinum–platinum/rhodium ^d	6	–200 to +1450

^a Usually 60% Cu, 40% Ni.

^b 90% Ni, 10% Cr.

^c 95% Ni plus Al, Si, Mn.

^d 90% Pt, 10% Rh.

11.2 International Temperature Scale of 1990

The experimental difficulties of accurate measurement of thermodynamic temperature with gas or other primary thermometers make it necessary for laboratories and standards institutions to have available a set of convenient practical thermometers whose behaviour is known in sufficient detail for them to be used for accurate interpolation between basic reference points whose thermodynamic temperatures have been determined with precision.

The basic idea of The international Temperature Scale of 1990 (ITS-90) is :

- Selection a set of reference points and assigns to these points values of thermodynamic temperature in the light of best available measurements,
- Selection a set of thermometers for interpolation between the reference points.

Range

3.0 K to 24.556 K	constant –volume gas thermometer
13.81 K to 903.89 K	platinum resistance thermometer
903.89 K to 1337.58 K	platinum/(platinum-10% rhodium) thermocouple
above 1337.58 K	radiation pyrometer

11.2 Fahrenheit Scale

The Fahrenheit temperature is related to the Celsius temperature by the equation

$$T_F = \frac{9}{5} T_c + 32 \quad (1.9)$$

REFERENCES:

[1] Çengel: Introduction to Thermodynamics and Heat Transfer, Second Edition

QUESTIONS:

- True thermodynamic equilibrium is attained in
 - Finite time
 - Infinite time
- Thermodynamic concern with the behaviour of the systems at happenings
 - microscopic level
 - macroscopic scale
- Energy of an isolated system can be altered
 - By doing work on the system
 - By extracting work from the system
 - By heating or cooling the system
 - Cannot be changed at all
- Two different objects are in thermal contact with one another. The objects are at different temperatures. The temperatures of the two objects determine
 - the process by which thermal energy is transferred.
 - the heat capacity of each object.
 - the direction of transfer of thermal energy between the objects.
 - the amount of internal energy in each object.
- What is the difference between extensive and intensive quantities?

Ans. Intensive properties do not depend on the amount of matter of the system but extensive properties do.

6. The specific weight (w) of a system is defined as the weight (W) divided by the volume (V), Is the specific weight an extensive or intensive property?

Ans. The specific weight is defined as:

$$w = \frac{W}{V}$$

If we were to divide the system into two halves, each half weighs $W/2$ and occupies a volume of $V/2$. The

specific weight of one of these halves is

$$w_2 = \frac{W/2}{V/2} = \frac{W}{V} = w$$

which is the same as the original specific weight. Hence, specific weight is an *intensive property*.

7. For a system to be in thermodynamic equilibrium, do the temperature and the pressure have to be the same everywhere?

8. **Ans.** For a system to be in thermodynamic equilibrium, the temperature has to be the same throughout but the pressure does not. However, there should be no unbalanced pressure forces present. The increasing pressure with depth in a fluid, for example, should be balanced by increasing weight.

9. What is the state postulate?

Ans. The State represent all the macroscopic properties (variables) associated with a system.

1.2. The limiting value of the ratio of pressures of a gas at the steam point and at the triple point of water when the gas is kept at constant volume is found to be 1.365954. What is the ideal-gas temperature of the steam point to six significant figures?

1.3. The resistance R' of a particular carbon resistor obeys the equation

$$\sqrt{\frac{\log R'}{T}} = a + b \log R',$$

where $a = -1.16$ and $b = 0.675$.

(a) In a liquid helium cryostat, the resistance is found to be exactly 1000Ω (ohms). What is the temperature?

1.4. The resistance of a doped germanium crystal obeys the equation

$$\log R' = 4.697 - 3.917 \log T.$$

(a) In a liquid helium cryostat, the resistance is measured to be 218Ω . What is the temperature?

1.9. What is the temperature on the Fahrenheit scale of the normal boiling point of H_2O , if this temperature is 99.974°C ? (Use five significant figures.)

Chapter 2

Simple thermodynamic Systems

2.1 Thermodynamic equilibrium

2.1 Thermodynamic equilibrium:

There are three types of thermodynamic equilibrium:

(I) Mechanical equilibrium: when there is no unbalanced force or torque in the interior of the system and also none between a system and surrounding, the system is said to be in mechanical equilibrium.

(II) Chemical equilibrium: Consider a system in mechanical equilibrium, and does not tend to undergoes changes in the internal structure such as **chemical reaction**, or **diffusion** (transfer of matter from one part of the system to another), then it is said to be in a state of chemical equilibrium.

(III) Thermal equilibrium: exist when there is no change in the coordinates of a system of mechanical and chemical equilibrium in spite of it is in a closed state. In other word there is no exchange of heat between the system and its surrounding, although the system in a closed state. In thermal equilibrium all the part of the system has the same temperature and this temperature is the same as that of surrounding. When this condition are not satisfied, a change of state will take place until new thermal equilibrium is reached.

When the three types of equilibrium is reached, the system is said to be in state of **thermodynamic equilibrium**. *Thermodynamic equilibrium can be described by macroscopic coordinates that do not involve the time, that is in terms of thermodynamic coordinates.*

When the condition for any one of the three types of equilibrium that constitute thermodynamic equilibrium are not satisfied , the system is said to be in **nonequilibrium state**. In this case there is no single pressure that refere to the system as a whole. Similarly there is no single temperature refere to the system as a whole. Therefore in the **nonequilibrium state the system can not described in terms of thermodynamic coordinates that describe the system as a whole.**

2.2 Equation of state:

Consider a system of constant mass of gas in thermodynamic equilibrium. In this case the thermodynamic variables (P, V, T) are not independent of one another, but constrained by the so-called equation of state.

$$f(P, V, T) = 0 \quad (2.1)$$

where f is a characteristic function of the system under study. It shows that, of the three directly measurable variables, P , V and T , only two are independent (Can take any arbitrary values) and the third is determined by the two others.

Example: For ideal gas (where there are no intermolecular attractions and the molecules themselves have no volume) the equation of state is

$$PV = nRT \quad (2.2)$$

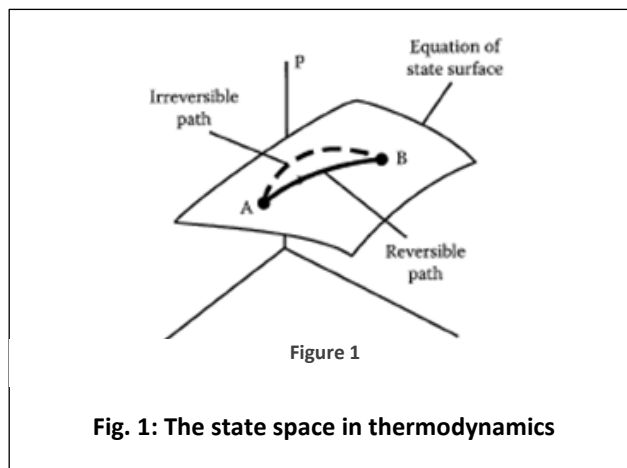
Here n is the number of moles present, $R = 8 \cdot 31 \frac{\text{J}}{\text{mol}\cdot\text{K}}$, is a constant called the universal gas constant, and T is the temperature in KELVINS. .

At high pressures, the equation of state is more complicated, and represented by van der Waals equation, which takes into account particles interactions and the finite size of the particles, Thus;

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad (2.3)$$

where a and b are constants that depend on the type of gas.

Geometrical representation of the equation of state: The equation of state of the ideal gas can be represented by a surface in the *state space* spanned by P , V , and T (see Fig. 1). All equilibrium states must be on this surface. f is a continuous, differentiable function, except at some special points.



Before we go further let me recall several useful relations which are valid for any Substance

$$R = kN_a, \quad n = \frac{N}{N_a}, \quad n = \frac{m}{M} \dots \dots (2.4)$$

where $k = 1.38 \times 10^{-23} \text{ J K}$ is Boltzmann's constant, N is the total number of molecules, $N_a = 6.02 \times 10^{23} \text{ mol}$ is (Avogadro number) the number of molecules in one mole of any substance, m is the mass of a substance, M is the **molar mass** (the mass of one mole) of a substance. The molar mass of a substance is numerically equal to the **molecular mass**, but expressed in mass units per mole, usually as g/mol (grams per mole) or kg/kmol. The molecular mass of a substance is the mass of one molecule of that substance, relative to the unified atomic mass unit (equal to 1/12 the mass of one atom of carbon-12). The **molecular mass can be calculated as the sum of the atomic masses of all the atoms of any one molecule.**

Example Problem (2.1):

(a) What is the volume of one mole of air at 0°C and atmospheric pressure.

(b) ; what is the density of air under the same conditions?

Solution: *We consider* the air under these conditions *as an ideal gas*

$$V = \frac{(1\text{mol})(8.31 \text{ J/mol} \cdot \text{K})(273\text{K})}{1.01 \times 10^5 \text{ N/m}^2} \approx 0.0224 \text{ m}^3 = 22.4 \text{ liters} .$$

From the ideal gas law $\rho = \frac{PM}{RT}$, where M is air molar mass. Air is a mixture of N_2

(78%), O_2 (21%), and Ar (1%), i.e. $M = 0.78 \times 28 + 0.21 \times 32 + 0.01 \times 40 = 29 \text{ kg/kmol}$.

$$\rho = \frac{(1.01 \times 10^5 \text{ N/m}^2)(29 \text{ kg/k mol})}{(8310 \text{ J/k mol} \cdot \text{K})(273\text{K})} = 1.29 \text{ kg/m}^3 .$$

Example Problem (2.2): A balloon of 700 liters contains 10 kmol of CO_2 at a temperature of 137 °C. Calculate the pressure in atmospheres inside the balloon from the ideal gas law and from the van der Waals equation if $a = 364 \times 10^3 \text{ J} \cdot \text{m}^3/\text{kmol}^2$, $b = 0.0427 \text{ m}^3/\text{kmol}$. What is the mass of CO_2 inside the balloon?

Solution: From the ideal gas law $P = \frac{nRT}{V}$,

$$P = \frac{(10 \text{ k mol})(8310 \text{ J/k mol} \cdot \text{K})(410 \text{ K})}{0.7 \text{ m}^3} \approx 487 \cdot 10^5 \text{ N/m}^2 \approx 482 \text{ atm};$$

From the van der Waals equation $P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$,

$$P = \frac{(10)(8310)(410)}{0.7 - (10)(0.0427)} - \frac{(364 \cdot 10^3) \cdot 10^2}{0.7^2} \approx 505 \cdot 10^5 \text{ N/m}^2 \approx 500 \text{ atm};$$

According to the definition, $m = nM$, $m = 10 \text{ k mol} \cdot (12 + 32) \text{ kg/k mol} = 440 \text{ kg}$.

It is obvious that no equation of states exists for the states traversed by a system that is not in mechanical and thermal equilibrium, since such states cannot be described in terms of thermodynamic coordinates referring to the system as a whole.

2.3 Hydrostatic systems

Simple systems: *are those systems that can be fully described by three thermodynamics coordinates X, Y, Z (XYZ systems).*

■ **The hydrostatic or PVT systems:** *is a type of the simple systems that can be described by the three coordinates P, V, T (PVT Systems). The hydrostatic systems exerts uniform hydrostatic pressure to the surrounding -sometimes is referred to as 'fluid system'*

Categories of hydrostatic systems:

1. **A pure substance:** *is a single chemical compound (e.g. H_2O) in a single phase or in a mixture of a solid, liquid, or gas phase.*
2. **A homogeneous mixture of different compound:** *such as a mixture of inert gasses, a mixture of active gasses, a mixture of liquid or, solution.*
3. **A heterogeneous mixture:** *such as a mixture of different gasses in contact with different liquids.*

Every hydrostatic system, that is, PVT system, has an equation of state that is valid for equilibrium states, as eq.(2.1). The equation of state for any coordinate can be solved in terms of the other two, thus consider the volume of V in terms of P, V

$$V = V(T, P)$$

The differential of V is written as;

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP, \dots \dots (2.5)$$

From the last equation we can define the following quantities:

➤ **Coefficient of Volume expansion, (Volume expansivity) β ,**

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \dots (2.6)$$

Note that: β is always positive, except for a few exceptions such as water between $0^\circ C$ and $4^\circ C$ experiences decrease in V with increasing T .

➤ **Bulk modulus, B**

$$B = -V \left(\frac{\partial P}{\partial V}\right)_T \dots \dots (2.6)$$

The inverse of B is called **compressibility, k**

$$k = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \dots (2.7)$$

Note that: *Volume expansivity, β , and the compressibility, k are of great use in thermodynamics, why?*

- **Because** the left side of eq. (2.) and eq.(2.) are experimentally measurable values, while the right side is theoretical values (partial derivatives). So, Measuring k and β allows us to get the change in thermodynamic coordinates which can not determine from the experiment.

Similarly, if the equation of state is solved for P and T , then we get

$$P = P(T, V) \quad \text{and} \quad T = T(V, P)$$

Which gives the partial differential equations

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV, \dots \dots (2.8)$$

$$dT = \left(\frac{\partial T}{\partial V}\right)_P dV + \left(\frac{\partial T}{\partial P}\right)_P dP, \dots \dots (2.9)$$

Consequently, the differential dP , dV , and dT in all the above equation are ***differentiale of actual functions and are called exact differentials.***

➤ ***Exact differential:*** dz is called an exact differential as a function of x, y if dz can be written as;

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \quad (2.10)$$

An infinitesimal that is not the differential of an actual function is called an ***inexact differential***

2.4 MATHEMATICAL THEORIES (The reciprocal and reciprocity theorems)

Suppose that three variable are related through the relation

$$f(x, y, z) = 0 \quad (2.11)$$

We may write the differential of dx and dy as;

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \dots \dots (2.12)$$

And

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \dots \dots (2.13)$$

Combining the two equations we get;

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left\{ \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \right\} + \left(\frac{\partial x}{\partial z}\right)_y dz \dots \dots (2.14)$$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left\{ \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y \right\} dz \dots \dots (2.15)$$

Choosing x and z as independent coordinates, the above is true for all the values of x and z . Thus if $dz = 0$ and $dx \neq 0$, then

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1 \dots \dots (2.16)$$

Or

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \dots \dots (2.17)$$

This is the ***reciprocal theorem*** which allows us to replace any partial derivative by the reciprocal of the inverted derivative with ***the same variable(s) held constant***.

If $dx = 0$ and $dz \neq 0$, then

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y = 0 \quad (2.18)$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = - \left(\frac{\partial x}{\partial z}\right)_y$$

(2.19)

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

This is ***the reciprocity theorem***. It may be written starting with any derivative then following through the other variables in cyclic order.

➤ **Applying the theorem to PVT system**

In the case of a PVT system, ***the reciprocity (cyclical) theorem*** yields the result

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y \Rightarrow \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V \quad (2.20)$$

By definition, ***the volume expansivity*** (eq.2) and ***the isothermal compressibility*** (eq.2) are

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \dots\dots (2.21)$$

$$k = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \dots (2.22)$$

$$\frac{\beta}{k} = \frac{\left(\frac{\partial V}{\partial T}\right)_P}{-\left(\frac{\partial V}{\partial P}\right)_T} = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T \quad (2.23)$$

But

$$\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V \quad (2.24)$$

Then

$$\frac{\beta}{k} = \left(\frac{\partial P}{\partial T}\right)_V \dots\dots (2.25)$$

➤ **dP in terms of β and k :**

Consider an infinitesimal change in P , then

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV \quad (2.26)$$

Then

$$dP = \frac{\beta}{k} dT - \frac{1}{kV} dV \dots \dots (2.27)$$

At $V = \text{constant}$

$$dP = \frac{\beta}{k} dT \quad (2.28)$$

For a **small change** in T from T_i to T_f , at constant volume, we can consider both β and k constant, and then the change in P from P_i to P_f , as

$$P_f - P_i = \frac{\beta}{k} \int_{T_i}^{T_f} dT$$

$$P_f - P_i = \frac{\beta}{k} (T_f - T_i) \quad (2.29)$$

From which the final pressure can be calculated.

Example problem (2.3): consider a mass of mercury at standard atmospheric pressure and a temperature 15°C is kept at constant volume. If the temperature is raised to 25°C , what will be the final pressure?.

Solution

$$\beta = 1.81 \times 10^{-4} \text{ K}^{-1},$$

and

$$\kappa = 4.01 \times 10^{-11} \text{ Pa}^{-1};$$

hence,

$$P_f - P_i = \frac{1.81 \times 10^{-4} \text{ K}^{-1} \times 10 \text{ K}}{4.01 \times 10^{-11} \text{ Pa}^{-1}}$$

$$= 4.51 \times 10^7 \text{ Pa},$$

and, since the initial atmospheric pressure is approximately $P_i = 1 \times 10^5 \text{ Pa}$, we have

$$P_f = 4.51 \times 10^7 \text{ Pa} + 0.01 \times 10^7 \text{ Pa}$$

$$= 4.52 \times 10^7 \text{ Pa} = 452 \text{ atm}.$$

Much of the development of thermodynamics has been based on the the hydrostatic or PVT system.

2.5 Stretched Wire

A wire can be thought of as a one –dimensional simple system. We know from the experimental results that the equilibrium states of the wire can be described by two independent variables of the following three coordinates:

1. The tension in the wire \mathcal{T} , measured in newtons (N)
2. The length of the wire L , measured in meters
3. The absolute temperature T , measured in kelvin (K)

This variables are connected through the the equation of states

$$g(\mathcal{T}, L, T) = 0 \dots\dots (2.30)$$

If the wire undergoes an infinitesimal change from one state of equilibrium to another, then the length can be written as a function of \mathcal{T} and T as;

$$L = L(\mathcal{T}, T)$$

Then dL is an exact differential and is written as

$$dL = \left(\frac{\partial L}{\partial T}\right)_{\mathcal{T}} dT + \left(\frac{\partial L}{\partial \mathcal{T}}\right)_T d\mathcal{T}$$

These derivatives are connected with very important physical quantities, in general physics,

➤ **The average coefficient of linear expansion, and linear expansivity**

$$\text{Average coefficient of linear expansion} = \frac{\text{change in length per unit length}}{\text{change of temperature}}$$

For infinitesimal change in temperature, we get an infinitesimal change in length, and then we can define the **linear expansivity, α** as;

$$\alpha = \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_T \dots \dots (2.31)$$

The linear expansivity α is in unit of reciprocal kelvin (K^{-1}).

In general physics, the **average Young's modulus** was defined as

$$\text{average Young's modulus} = \frac{\text{change in tension per unit area}}{\text{change of Length per unit length}}$$

For infinitesimal change in tension, we can define the **isothermal Young's modulus, Y** as;

$$Y = \frac{L}{A} \left(\frac{\partial \mathcal{T}}{\partial L} \right)_T \dots \dots (2.32)$$

Where A denote the cross-section area of the wire.

Note That:

- Y is always positive
- Y depend mostly in teperature and is constant for a small te,perature range
- The unit of Y is (N/m^2)

Using the cyclical theory , then

$$\left(\frac{\partial \mathcal{T}}{\partial L} \right)_T \left(\frac{\partial L}{\partial T} \right)_T \left(\frac{\partial T}{\partial \mathcal{T}} \right)_L = -1$$

$$\left(\frac{\partial \mathcal{J}}{\partial T}\right)_L = -\left(\frac{\partial \mathcal{J}}{\partial L}\right)_T \left(\frac{\partial L}{\partial T}\right)_L$$

$$\left(\frac{\partial \mathcal{J}}{\partial T}\right)_L = -\frac{YA}{L} \alpha L$$

So

$$\left(\frac{\partial \mathcal{J}}{\partial T}\right)_L = -AY\alpha \dots \dots (2.33)$$

Questions

- 1- Is the number of moles of a substance contained in a system an extensive or intensive property?

Problems

2.1. The equation of state of an ideal gas is $PV = nRT$, where n and R are constants.

(a) Show that the volume expansivity β is equal to $1/T$.

(b) Show that the isothermal compressibility κ is equal to $1/P$.

Answer

- (a) Given equation of state for a ideal gas

$$PV = nRT, \quad \text{Eq. (1)}$$

and the definition of volume expansivity $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)$, it is easily verified that $\beta = 1/T$ by taking the partial derivate of Eq. (1) with respect to T :

$$\frac{\partial}{\partial T} (PV = nRT) \rightarrow P \frac{\partial V}{\partial T} = nR \quad \text{Eq. (2)}$$

Inserting $PV = nRT$ into Eq. (2), we arrive at

$$\frac{\partial V}{\partial T} = \frac{nR}{P} = \frac{PV}{T} \frac{1}{P} = \frac{V}{T}$$

Hence, $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right) = \beta = \frac{1}{V} \left(\frac{V}{T} \right) = \frac{1}{T}$.

(b)

Given equation of state for a ideal gas

$$PV = nRT, \quad \text{Eq. (1)}$$

and the definition of isothermal compressibility $\kappa = \frac{1}{B} = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)$, it is easily verified that $\beta = 1/P$ by taking the partial derivate of Eq. (1) with respect to P :

$$\frac{\partial}{\partial P} (PV = nRT) \rightarrow P \frac{\partial V}{\partial P} + V = \frac{\partial}{\partial P} (nRT) = 0 \quad \text{Eq. (2)}$$

Inserting $PV = nRT$ into Eq. (2), we arrive at

$$\frac{\partial V}{\partial P} = -\frac{V}{P}$$

Hence, $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right) = -\frac{1}{V} \left(-\frac{V}{P} \right) = \frac{1}{P}$.

2.2. The equation of state of a van der Waals gas is given as

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

where a , b , and R are constants. Calculate the following quantities:

(a) $(\partial P/\partial v)_T$;

(b) $(\partial P/\partial T)_v$.

From parts (a) and (b) calculate $(\partial v/\partial T)_P$.

Answer

Problem 2.2: Given the equation of state of a van der Waals gas, $\left(P + \frac{a}{v^2}\right)(v - b) = RT$:

(a) Taking the partial derivative with respect to v , with constant T ,

$$\frac{\partial}{\partial v} \left[\left(P + \frac{a}{v^2} \right) (v - b) \right] = \frac{\partial}{\partial v} (RT) = 0$$

$$(v - b) \frac{\partial}{\partial v} \left(P + \frac{a}{v^2} \right) + \left(P + \frac{a}{v^2} \right) \frac{\partial}{\partial v} (v - b) = 0$$

$$(v - b) \left(\frac{\partial P}{\partial v} - \frac{2a}{v^3} \right) + \left(P + \frac{a}{v^2} \right) = 0$$

$$\frac{\partial P}{\partial v} = - \frac{P + \frac{a}{v^2}}{v - b} + \frac{2a}{v^3}$$

(b) Taking the partial derivative with respect to T , with constant v ,

$$\frac{\partial}{\partial T} \left[\left(P + \frac{a}{v^2} \right) (v - b) \right] = \frac{\partial}{\partial T} (RT)$$

$$(v - b) \frac{\partial}{\partial T} \left(P + \frac{a}{v^2} \right) + \left(P + \frac{a}{v^2} \right) \frac{\partial}{\partial T} (v - b) = R$$

$$(v - b) \left[\frac{\partial P}{\partial T} + a \frac{\partial}{\partial T} \left(\frac{1}{v^2} \right) \right] + \left(P + \frac{a}{v^2} \right) \frac{\partial v}{\partial T} = R$$

$$(v - b) \left(\frac{\partial P}{\partial T} + 0 \right) + \left(P + \frac{a}{v^2} \right) \cdot 0 = R$$

$$\frac{\partial P}{\partial T} = \frac{R}{v - b}$$

(c) From

$$\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_v$$

$$\rightarrow \left(\frac{\partial v}{\partial T}\right)_P = \frac{-\left(\frac{\partial P}{\partial T}\right)_v}{\left(\frac{\partial P}{\partial v}\right)_T} = -\frac{\frac{R}{v-b}}{-\frac{P+\frac{a}{v^2}}{v-b} + \frac{2a}{v^3}} = \frac{R}{\frac{a}{v^2} - \frac{2ab}{v^3} - P}$$

Chapter 3

Work

3 Work

3.1 Work

3.2 Quasi-Static Process

3.3 Work in Changing the Volume of a Hydrostatic System

3.4 PV Diagram

3.5 Hydrostatic Work Depends on the Path

3.6 Calculation of $\int P dV$ for Quasi-Static Processes

3.7 Work in Changing the Length of a Wire

3.8 Work in Changing the Area of a Surface Film

3.9 Work in Moving Charge with an Electrochemical Cell

3.10 Work in Changing the Total Polarization of a Dielectric Solid

3.11 Work in Changing the Total Magnetization of a Paramagnetic Solid

3.12 Generalized Work

3.13 Composite Systems

3.1 WORK

Qualitatively: At any time, an object undergoes a displacement under the action of force, work is said to be done.

Quantitatively; work is the product of the force and the component of displacement parallel to the force.

There are Two kinds of work

- i) **External Work:** As a result of interaction between the system and its surrounding (e.g. a gas confined cylinder when expand does external work on its surrounding).
- ii) **Internal Work:** As a result of interactions between different parts of the system (e.g. the interactions at the microscopic scales between molecules, atoms, or electrons on one another).

We will confine our attention to the external work.

Sign convention:

- Work is positive when done **on** the system
- Work is negative when done **by** the system.

3.2 QUASI-STATIC PROCESS

We introduced the concept of quasi–static process in chapter 1. Here, we want to redefine this process more precisely:

- **The quasistatic process :** is an **ideal** case in which the external forces acting on a system are varied only slightly, and the process proceeds infinitesimally slowly.

The quasistatic process has the following features:

- i) During this process, the system is in all times infinitesimally near a state of thermodynamic equilibrium. This means we can get equation of state describe the system as a whole.
- ii) The quasistatic process is equivalent to reversible process.

Now we will discuss the quasistatic process in those systems that we discussed in the previous chapter:

3.3 WORK IN CHANGING THE VOLUME OF A HYDROSTATIC SYSTEM:

As shown in the figure, consider quasi-static compression of a hydrostatic system enclosed by an adiabatic cylinder and piston.

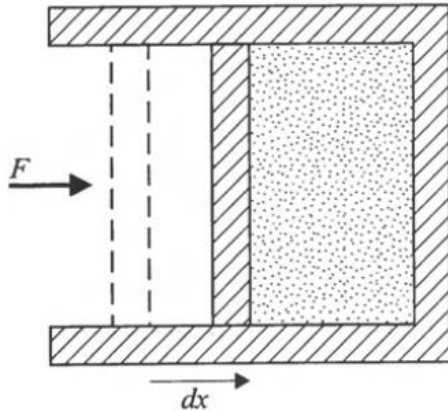


FIGURE 3-1
Quasi-static compression of a hydrostatic system enclosed by an adiabatic cylinder and piston.

- The pressure exerted **by the system** at the internal face of the piston is P . Therefore, the force on the internal face of the piston is PA (A is the cross-section area of the cylinder).
- The surrounding exerts an external force F on the external face of the piston.
- If F increased slightly the force PA of the system, then the piston will move infinitesimal distance dx during compression, as shown in the Fig.3-1.
- The work done by the external force during this displacement is ;

$$dW = Fdx = PAdx \quad (2.1)$$

But during compression the volume of the system decreases, so

$$Adx = -dV \quad (2.2)$$

Then

$$dW = -PdV \dots \dots (2.3)$$

- **The convention** is that **work done on the system** increases the energy of the system and **work done by the system** decrease the energy of the system.
- Therefore, the minus sign before PdV ensures that negative dV (a compression) gives rise **a positive work done on** the system, and conversely positive dV (expansion) gives rise **a negative work done by** the system.

(The SI unit of work is Joule (J))

In a *finite* quasi-static process the work done by a system in expansion from initial volume V_i to a larger volume V_f is expressed as

$$W_{if} = - \int_{V_i}^{V_f} PdV \quad (2.4)$$

and in contracting from state f to state i , **along the same path of integration** but in opposite direction , the work done on the system is

$$W_{fi} = - \int_{V_f}^{V_i} P dV \quad (2.5)$$

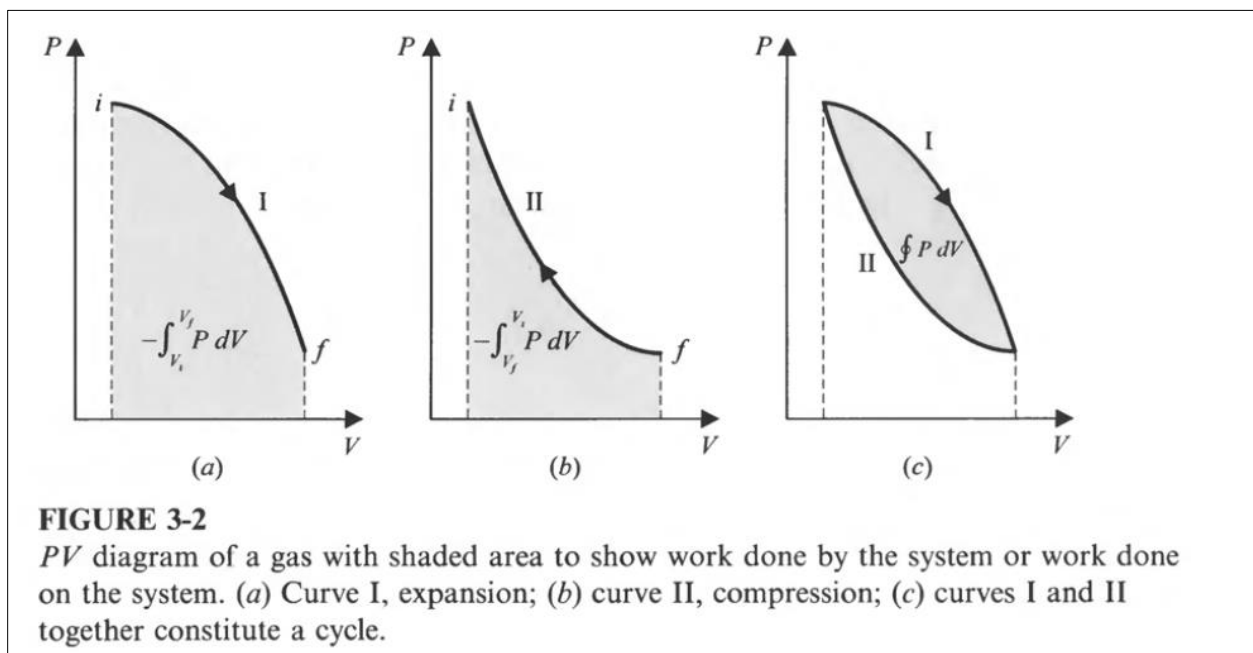
So over quasi-static path , we have

$$W_{if} = -W_{fi} \quad (2.6)$$

3.4 PV DIAGRAM

Consider the process of compression or expansion of the hydrostatic system shown in figure 3-1 . The resulting diagram in which pressure is plotted along y-axis and the volume along x-axis, is called a *PV diagram*.

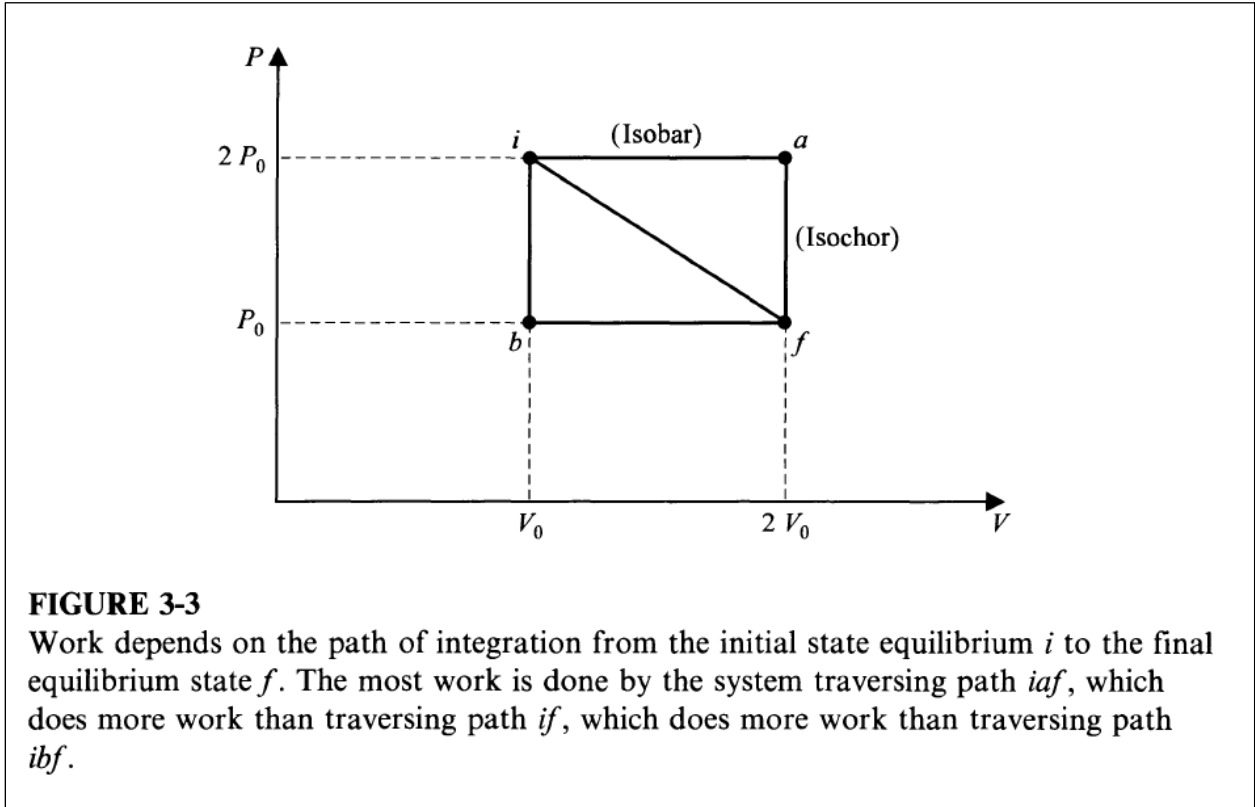
- The area under the PV curve represents the work done by or on the system



- Figure 3-2(a) shows expansion process (curve I). The integral $- \int_{V_i}^{V_f} P dV$ is **negative**, i.e. the work is done **by** the system.
- Figure 3-2(b) shows compression process (curve II). The integral $- \int_{V_f}^{V_i} P dV$ is **positive**, i.e. the work is done **on** the system.
- Figure 3-2(c) shows the two curves I and II together. Such a series of two or more process represent by a closed figure is called **a cycle**. The net work done in a cycle is the difference between the area under curve I and curve II.

3.5 HYDROSTATIC WORK DEPENDS ON THE PATH

As shown in the figure below, the paths iaf , and ibf , has a different area. Then they have a different work.



- This means that, *the work done by a system depends not only on the initial and final states but also on the path of integration*. Consequently, the work is **inexact differential** (*i.e. the work is not state function*).

3.6 CALCULATION OF $\int P dV$ FOR QUASI-STATIC PROCESSES

i. *Quasi-static isothermal expansion or compression of an ideal gas*

$$W = - \int_i^f P dV = - \int_i^f \frac{nRT}{V} dV = -nRT \int_i^f \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i} \quad (2.7)$$

Example :

Let us calculate the work in compressing 2 mol of an ideal gas kept at a constant temperature of 20°C from a volume of 4 liters to 1 liter. Then, we have $n = 2 \text{ mol}$, $R = 8.315 \text{ J/mol} \cdot \text{K}$, $T = 293 \text{ K}$, $V_i = 4 \times 10^{-6} \text{ m}^3$, and $V_f = 1 \times 10^{-6} \text{ m}^3$. Thus,

$$\begin{aligned} W &= -(2 \text{ mol})(8.315 \text{ J/mol} \cdot \text{K})(293 \text{ K})(\ln \frac{1}{4}) \\ &= 6753 \text{ J.} \end{aligned}$$

The positive value of W indicates that work was done *on* the gas.

ii) *Quasi-static isothermal increase of pressure on a solid*

Suppose the pressure of on 10g of cooper increased quasi-statically and isothermally at 20°C from 0 to 100 atm. What is the work done during this process?

Answer:

$$W = - \int P dV \quad (2.8)$$

But

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \quad (2.9)$$

And since

$$k = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \quad (2.10)$$

Then

$$dV = -kVdp \quad (2.11)$$

Substituting this result for dV in the expression for work, then

$$W = \int PkVdp \quad (2.12)$$

At constant temperature, k and V are practically constant , then

$$W = \frac{kV}{2}(P_f^2 - P_i^2) \quad (2.13)$$

Example

For copper at 20°C, $\rho = 8.96 \times 10^3 \text{ kg/m}^3$, $\kappa = 7.16 \times 10^{-12} \text{ Pa}^{-1}$, $m = 10^{-2} \text{ kg}$, $P_i = 0$, and $P_f = 1000 \text{ atm} = 1.01 \times 10^8 \text{ Pa}$. Hence,

$$\begin{aligned} W &= \frac{(10^{-2} \text{ kg})(7.16 \times 10^{-12} \text{ Pa}^{-1})(1.01 \times 10^8 \text{ Pa})^2}{2(8.96 \times 10^3 \text{ kg/m}^3)} \\ &= 0.408 \times 10^1 \text{ Pa} \cdot \text{m}^3 \\ &= 4.08 \text{ J}. \end{aligned}$$

The positive value of W indicates that work was done *on* the copper.

Note That: A little work was done in raising the pressure on the copper compared with the work in compressing the gas in the first example. The reason is that the volume of copper changed very little. So in compressing the gas we can usually neglect the work done on the material of the container.

PROBLEMS

Problem 3.1

Show that the work done by an ideal gas during the quasi-static, isothermal expansion from an initial pressure V_i to a final pressure V_f , is given by

$$W = -nRT \ln (V_f/V_i).$$

Solution

$$W = - \int_i^f PdV = - \int_i^f \frac{nRT}{V} dV = -nRT \int_i^f \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

Problem 3.2

(a) Show that the work done by an ideal gas during the quasi-static, isothermal expansion from an initial pressure P_i to a final pressure P_f , is given by

$$W = nRT \ln (P_f/P_i).$$

Solution:

For isothermal process

$$P_i V_i = P_f V_f.$$

Hence

$$V_f/V_i = P_i/P_f.$$

Substitute this into

$$W = -RT \ln (V_f/V_i).$$

Then

$$W = -nRT \ln (P_i/P_f) = nRT \ln (P_f/P_i).$$

Problem 3.3

An adiabatic chamber with rigid walls consists of two compartments, one containing a gas and the other evacuated; the partition between the two compartments is suddenly removed. Is the work done during an infinitesimal portion of this process (called an adiabatic expansion) equal PdV ?

Answer: NO. Because there is no work done against the expansion of the gas-filled compartment by the evacuated compartment. During **a free expansion** of a gas, **the heat transfer between the system and the surrounding, and the work done by the gas are both equals to zero**. In other words, no work is done by the gas during a free expansion.

Problem 3.4

- (a) Calculate the work done upon expansion of 1 mol of gas quasi-statically and isothermally from volume v_i to volume v_f , when the equation of state is $\left(P + \frac{a}{v^2}\right)(v-b) = RT$, where a and b are the van der Waals constant.
- (b) If $a = 1.4 \times 10^9 \text{ N}\cdot\text{m}^4/\text{mol}$ and $b = 3.2 \times 10^{-5} \text{ m}^3/\text{mol}$, how much work is done when the gas expands from a volume of 10 liters to a volume of 22.4 liters at 20°C ?

Solutions: (a)

$$P = \frac{RT}{(v-b)} - \frac{a}{v^2}$$

$$W = - \int_{v_i}^{v_f} P dv$$

$$(b) \quad = \int_{v_i}^{v_f} \frac{-RT}{(v-b)} + \frac{a}{v^2} dv = \left[\frac{RT}{(v-b)^2} - \frac{2a}{v^3} \right]_{v_i}^{v_f}$$

$$W = \left[\frac{8.31(293)}{(v - 3.2 \times 10^{-5})^2} - \frac{2(1.4 \times 10^9)}{v^3} \right]_{0.01}^{0.0224} = 2.25 \times 10^{15} \text{ J}$$

CHAPTER 4

Heat and the First Law of Thermodynamics

The first law of thermodynamics is essentially an extension of the principle of the **conservation of energy** to include systems in which there is **flow of heat**. Historically, it marks the recognition of heat as a form of energy.

4.1 WORK AND HEAT

- In chapter 3 we saw how system can transfer from initial state to final state via quasi-static process by doing a work (figure 4-1 a,b). Also, we explained how the work done during the process could be calculated.
- However, there are other means for changing the state of the system do not necessary involve the performance of a work. By absorbing (or releasing) heat (figure 4-1 c,d).

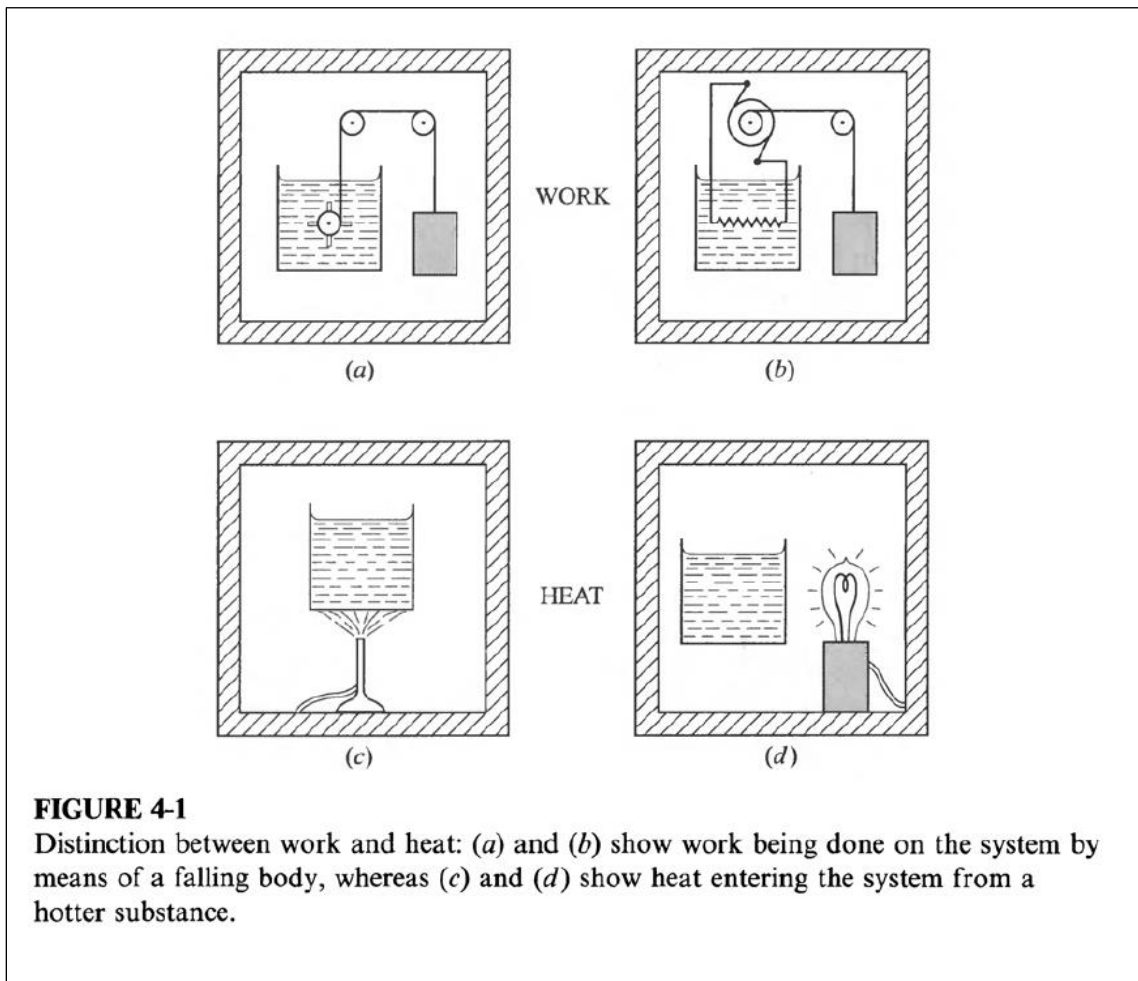


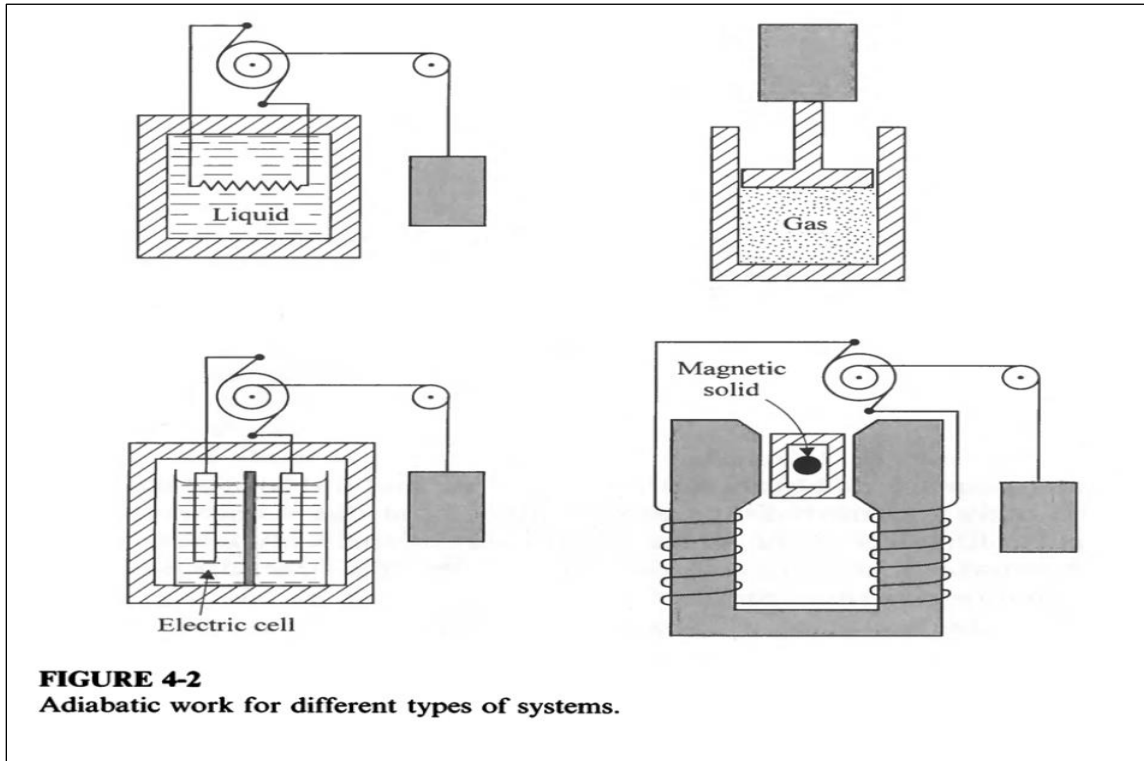
FIGURE 4-1

Distinction between work and heat: (a) and (b) show work being done on the system by means of a falling body, whereas (c) and (d) show heat entering the system from a hotter substance.

Definition: Heat is a form of energy that transfer between a system and its environment because of the different in temperature only.

4.2 ADIABATIC WORK

When a closed system confined within an *adiabatic boundary* allowing *no heat to* penetrate, as shown in figure 4.2, the system may still be coupled to the surrounding so that work may be done.



- **Path independent adiabatic work:**

figure 4.2, shows a series of experiments which show that the system can be changed from initial state to the *same* final state by the performance of *adiabatic work* only through a different paths.

- path I:** The state of composite *electrical* system, composed of a resistor immersed in water, is changed from an initial state *i* of ($P_i = 1 \text{ atm}, T_i = 287.7 \text{ K}$), to a final state *f* of ($P_f = 1 \text{ atm}, T_f = 288.7 \text{ K}$), by passing a current through the resistor from, as shown in figure 4-3.

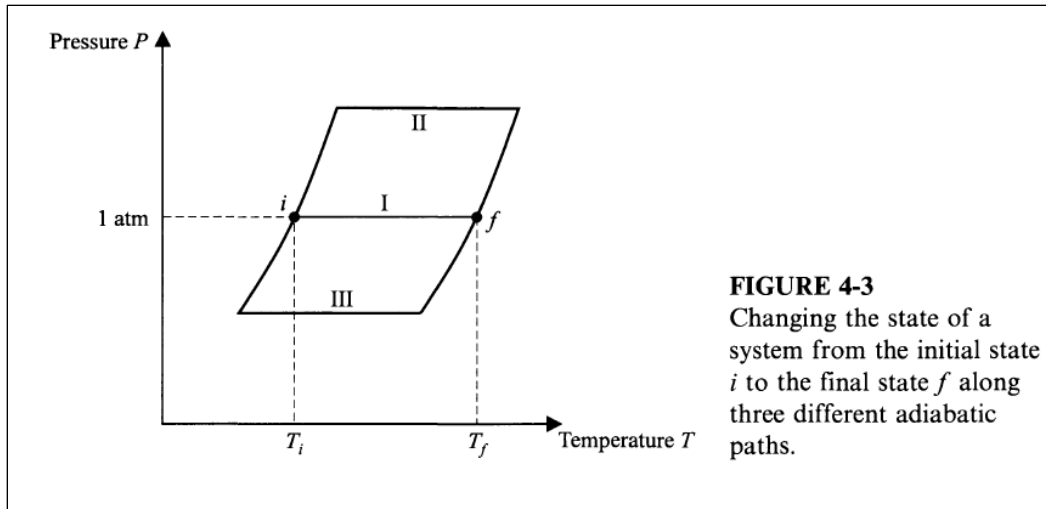


FIGURE 4-3
Changing the state of a system from the initial state i to the final state f along three different adiabatic paths.

- ii) **path II**, the system is changed from the state i to the state f by compressing the water adiabatically from i to a , then use a current in a resistor from a to b and then expand from b to f .
- iii) **path III** is another path to reach by the system from the state i to the state f .

In conclusion: there are an infinite number of paths by which a system may be transferred from initial state to a final state by performance of adiabatic work only. *The generalization of this rule is a statement for the first law of thermodynamic.*

If a closed system is caused to change from an initial state to a final state by adiabatic means only, then the work done on the system is the same for all adiabatic paths connecting the two states.

The path independent work follow from the *restricted* statement of the first law of thermodynamic ensures the existence of a function of the thermodynamic coordinates of the system whose value at the final state minus its value at the initial state equal the adiabatic work done during this change. This function is called *the internal energy function, U* . Then we have

$$W_{i \rightarrow f} = U_f - U_i \dots \dots (4 \cdot 1)$$

If $W_{i \rightarrow f} > 0$, then $U_f > U_i$

4.3 INTERNAL ENERGY AS A STATE FUNCTION

Now it is shown that the change in the internal energy is path independent. This means that U is *a state function*. It was clear in chapter two that the equilibrium state of hydrostatic system, which is described by three coordinates P, V , and T , can be *totally* determined by two coordinates, and the third is fixed by the equation of state.

Then the infinitesimal change in the internal energy dU is *an exact differential*. Which means that, *if U is a function of V and T for hydrostatic system, then dU is given as*

$$dU(T, V) = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV,$$

Or if we considered U as a function of T and P , then

$$dU(T, P) = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP.$$

Note that :

$$\left(\frac{\partial U}{\partial T}\right)_V \neq \left(\frac{\partial U}{\partial T}\right)_P$$

They have a different meaning as we will see later

4.4 MATHEMATICAL FORMULATION OF THE FIRST LAW

We have been considering processes during which a system undergoes a change of state through the performance of adiabatic work only. *in this case it is cleared as given in eq.(4.1) that $\Delta U = U_f - U_i = W_{i \rightarrow f}$*

- *Equation (4.1) applies to adiabatic processes.*
- However, we know that it is also possible to change the state of a system without doing work on it (We may use heat alone) or any combination of heat and work. Thus, when a system is not thermally isolated equation (4.1) is no longer valid. It must now be modified to

$$\Delta U = U_f - U_i = Q + W \dots \dots (4 \cdot 2)$$

Where Q is the heat add to the system . Like internal energy and work heat is measured in Joules in the SI unit of system.

Equation (4 · 2) is the mathematical form of the first law of thermodynamics. This formula contains three relateds idea

- 1- *The existence of the internal energy function*
- 2- *The principle of conservation of energy*
- 3- *The definition of heat as energy in transit by virtue of temperature difference.*

Note that

Heating is a process by which there is an exchange of energy between system and its surrounding because of temperature difference.

But what is the energy that exchange?

The answer depend on the condition of process.

- In *isochoric* process of hydrostatic system (constant volume process), the heat transferred is simply *the internal energy*.
- In *isobaric* process of hydrostatic system (constant pressure process) , the heat transferred is *enthalpy, which is another state function*, which is a type of energy, as we will see later.

4.5 THE CONCEPT OF HEAT

Note that

As we have defined the heat as “ *heat is either internal energy or enthalpy in transit*” because of difference in temperature.

consequently

1. When the flow of heat has stopped we can not use the word of heat at all. **So, it is not correct to refer to the heat of body.**
2. *The heat and the work done on or by the system is not a function of the coordinates of the system (they are not a state function or exact differential) , So infinitesimal amount of heat and work is written as dW or as dQ (read d bar W or d bar Q).*

Example : (The method of mixture)

Consider two systems A, and B with different temperatures and in thermal contact. Consider the composite system is surrounded by adiabatic walls.

Prof that

$$Q_A = -Q_B \dots (4.3)$$

where Q_A is heat gained or lost by system A, and Q_B is the heat gain or lost by system B.

Answer

Applying the first law of thermodynamics to system A and system B we have

$$U_{Af} - U_{Ai} = Q_A + W_A \quad (4.4)$$

$$U_{Bf} - U_{Bi} = Q_B + W_B \quad (4.5)$$

Adding the two equations we get

$$(U_{Af} + U_{Bf}) - (U_{Ai} + U_{Bi}) = (Q_A + Q_B) + (W_A + W_B) \quad (4.6)$$

But

$(U_{Af} + U_{Bf}) - (U_{Ai} + U_{Bi})$ is the change in the internal energy of the composite system

and $(W_A + W_B)$ is the work done on the composite system.

Then

$(Q_A + Q_B)$ is the heat added to the composite system.

But the composite system is surrounded by adiabatic walls, the

$$(Q_A + Q_B) = 0$$

Then

$$Q_A = -Q_B \dots (4.7)$$

Note that :

Equation (3.4) is the basis for calculating the final temperature when a piece of hot metal dropped into a cold water contained in calorimeter.

4.6 DIFFERENTIAL FORM OF FIRST LAW

For infinitesimal change on the coordinates of the system, the first law of thermodynamics is written as;

$$dU = dQ + dW \dots\dots\dots (4.8)$$

For an infinitesimal quasi-static process of a hydrostatic system, the first law of thermodynamic can be written as

$$dU = dQ - PdV \dots\dots (4 \cdot 9)$$

Where $dW = -PdV$

4.7 HEAT CAPACITY AND ITS MEASUREMENTS

If a system experience a change of temperature from T_i to T_f during the transfer of Q units of heat, *the average heat capacity* of the system is defined as;

$$\text{Average heat capacity} = \frac{Q}{T_f - T_i} \quad (4.10)$$

When Q and $T_f - T_i$ becomes infinitesimal, then this ratio approach limiting value, known as the *heat capacity* C , thus

$$C = \lim_{T_f \rightarrow T_i} \frac{Q}{T_f - T_i}$$

Or

$$C = \frac{dQ}{dT} \dots\dots (4.11)$$

Where heat is measured on Joule per kelvin (J /K) in SI unit.

- **The Specific heat**

The heat capacity is an *extensive* quantity, it depend on the mass of the system. So, it is better to use *the specific heat c* as an Intensive *quantity*, which is given as;

$$c = \frac{C}{m} = \frac{1}{m} \frac{dQ}{dT} \quad (4.12)$$

Where m is the mass of the system

c is measured in Joule per kilogram-Kelvin (J/kg·K)

- **Molar specific heat**

We can also define *molar specific heat*, which is defined as

$$\text{Molar specific heat} = \frac{C}{n} = \frac{1}{n} \frac{dQ}{dT} \quad (4.13)$$

Where n is the number of moles contained on the system.

Molar specific heat is measured on (J/mol·K).

Depending on the process which the system undergoes, two type of heat capacity can be defined

- **The heat capacity at constant volume C_V**

$$C_V = \left(\frac{dQ}{dT} \right)_V \dots\dots (4 \cdot 14)$$

- **The heat capacity at constant pressure**

$$C_P = \left(\frac{dQ}{dT} \right)_P \dots\dots (4 \cdot 15)$$

In general C_V and C_P are different

4.8 SPECIFIC HEAT OF WATER ; THE CALORIE

Calorie (abbreviation Cal) is : *The amount of heat required to raise the temperature of 1 g of water from 14.5°C to 15.5°C.*

4.9 EQUATIONS FOR HYDROSTATIC SYSTEM

The mathematical formulation for the first law of hydrostatic system is

$$dQ = dU + pdV \quad (4.16)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV.$$

Therefore, the first law becomes

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV. \quad (4.17)$$

Dividing by dT , we get

$$\frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \frac{dV}{dT}. \quad (4.18)$$

This equation is true for *any* process involving any temperature change dT and any volume change dV .

1. If V is constant, then $dV = 0$, and

$$\left(\frac{dQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V. \quad (4.19)$$

Where U is a function of P , V , and T . Choosing T and V , then we have

But

$$C_V = \left(\frac{dQ}{dT}\right)_V$$

Then

$C_V = \left(\frac{\partial U}{\partial T}\right)_V \dots\dots (4.20)$
--

2. If P is constant, then Eq. (4.12) becomes

$$\left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \left(\frac{\partial V}{\partial T}\right)_P. \quad (4.20)$$

But, by definition $(dQ/dT)_P = C_P$ and also $(\partial V/\partial T)_P = V\beta$ from Eq. (2.3). Hence,

$$C_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] V\beta,$$

or

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_P - C_V}{V\beta} - P. \quad (4.21)$$

Although this equation is not important in its present form, it is a good example of an equation that relates a quantity $(\partial U/\partial V)_T$, which is ordinarily not measured, with state functions such as C_P , C_V , and β , which can be measured.

4.10 QUASI-STATIC FLOW OF HEAT, HEAT RESERVIOR

- A heat reservoir : is A body of such a large mass that it may absorbed or reject an unlimited quantity of heat without experiencing an appreciable change in temperature or in any other thermodynamic coordinate.

The ocean and atmosphere is example for heat reservoir.

mal. The flow of heat will be quasi-static and can be calculated as follows from the definition of C_P :

$$C_P = \left(\frac{dQ}{dT}\right)_P,$$

and, therefore, for a quasi-static isobaric process, a path of integration is prescribed, so

$$Q_P = \int_{T_i}^{T_f} C_P dT. \quad (4.22)$$

For example, the heat absorbed by water from a series of reservoirs varying in temperature from T_i to T_f during a quasi-static isobaric process is calculated from Eq. (4.15). Assume C_P remains practically constant, integrate, and then

$$Q_P = C_P(T_f - T_i).$$

For a quasi-static isochoric process, another path of integration is prescribed, so

$$Q_V = \int_{T_i}^{T_f} C_V dT. \quad (4.23)$$

Similar considerations hold for other systems during quasi-static processes.

Problems

- 4.1 A combustion experiment is performed by burning a mixture of fuel and oxygen in a constant-volume container surrounded by a water bath. During the experiment, the temperature of the water rises. If the system is the mixture of fuel and oxygen:
- Has heat been transferred?
 - Has work been done?
 - What is the sign of ΔU ?
- 4.2 A liquid is irregularly stirred in a well-insulated container and thereby experiences a rise in temperature. If the system is the liquid:
- Has heat been transferred?
 - Has work been done?
 - What is the sign of ΔU ?
- 4.3 The amount of water in a lake may be increased by action of underground springs, by inflow from a river, and by rain. It may be decreased by various outflows and by evaporation.
- Comment on the question: How much rain is there in the lake?
 - Comment on the question: How much water in the lake is due to rain?
 - What concept is analogous to “rain in the lake”?
- 4.4 A container with rigid well-insulated walls is divided into two parts by a partition. One part contains a gas, and the other is evacuated. If the partition suddenly breaks, show that the initial and final internal energies of the gas are equal. (*Note: this process is called an adiabatic free expansion.*)

4.5 Regarding the internal energy of a hydrostatic system to be a function of T and P , derive the following equations:

$$(a) \quad dQ = \left[\left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \right] dT + \left[\left(\frac{\partial U}{\partial P} \right)_T + P \left(\frac{\partial V}{\partial P} \right)_T \right] dP.$$

$$(b) \quad \left(\frac{\partial U}{\partial T} \right)_P = C_P - PV\beta.$$

$$(c) \quad \left(\frac{\partial U}{\partial P} \right)_T = PV\kappa - (C_P - C_V) \frac{\kappa}{\beta}.$$

Solution

a) Let $U = U(P, T)$, then

$$dU = \left(\frac{\partial U}{\partial P} \right)_T dP + \left(\frac{\partial U}{\partial T} \right)_P dT$$

The first law of thermodynamics is

$$du = dQ - PdV$$

Combining the two equations

$$dQ = \left(\frac{\partial U}{\partial T} \right)_P dT + \left(\frac{\partial U}{\partial P} \right)_T dP + PdV \quad (1)$$

For a PVT system, we can write V as a function of T and P .

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP$$

By substituting the expression of dV into equation Eq. (1), we get

$$dQ = \left[\left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \right] dT + \left[\left(\frac{\partial U}{\partial P} \right)_T + P \left(\frac{\partial V}{\partial P} \right)_T \right] dP$$

(b) For a PVT system, we can write V as a function of T and P .

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP$$

By substituting the expression of dV into equation Eq. (1), we get

$$dQ = \left[\left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \right] dT + \left[\left(\frac{\partial U}{\partial P} \right)_T + P \left(\frac{\partial V}{\partial P} \right)_T \right] dP$$

At constant pressure, $dP=0$. Setting $dP=0$, and dividing Eq. (2) by dT , we get

$$\left. \frac{dQ}{dT} \right|_P \equiv C_p = \left[\left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \right] dT$$

But

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

Then

$$C_p = \left(\frac{\partial U}{\partial T} \right)_P + PV\beta$$

(c) At constant volume, $dV=0$. Setting $dV=0$, and dividing Eq.(1) by dT , we get

$$dQ = \left(\frac{\partial U}{\partial T} \right)_P dT + \left(\frac{\partial U}{\partial P} \right)_T dP + PdV$$

$$\left. \frac{dQ}{dT} \right|_V \equiv C_v = \left(\frac{\partial U}{\partial T} \right)_P + \left(\frac{\partial U}{\partial P} \right)_T \left. \frac{dP}{dT} \right|_V = \left(\frac{\partial U}{\partial T} \right)_P + \left(\frac{\partial U}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_V ;$$

where

$$\left. \frac{dP}{dT} \right|_V = \left(\frac{\partial P}{\partial T} \right)_V$$

But

$$\left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial V}{\partial P} \right)_T = -1$$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \Rightarrow V = \frac{1}{\beta} \left(\frac{\partial T}{\partial V} \right)_P \Rightarrow \left(\frac{\partial T}{\partial V} \right)_P = \beta V$$

but

$$\kappa = \frac{-1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{\beta}{\kappa}$$

$$\frac{dq}{dT} = \left(\frac{\partial u}{\partial T}\right)_v + \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right] \frac{dv}{dT} \quad (4), \text{ and} \quad c_p = \left(\frac{\partial U}{\partial T}\right)_P + PV\beta \quad \blacksquare \quad \text{Combining Eq. (3),}$$

Then

$$C_v = (C_p - \beta PV) + \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\beta}{\kappa}\right) \Rightarrow \frac{C_v - C_p + \beta PV}{\left(\frac{\beta}{\kappa}\right)} = \left(\frac{\partial U}{\partial P}\right)_T$$

4.6 One mole of a gas obeys the van der Waals equation of state:

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

and its molar internal energy is given by

$$u = cT - \frac{a}{v},$$

where a , b , c , and R are constants. Calculate the molar heat capacities c_V and c_P .

Solution

$$\text{Let } u = u(T, v)$$

Then

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv \quad (1)$$

$$dq = du + Pdv \quad (2)$$

Eq. (1) combined with Eq. (2) then

$$dq = \left(\frac{\partial u}{\partial T}\right)_v dT + \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right] dv$$

Divided by dT then,

(5)

At constant volume we have

$$\left. \frac{dq}{dT} \right|_v \equiv c_V = \left(\frac{\partial u}{\partial T} \right)_v = c, \text{ since } u = cT - a/v$$

■ At constant pressure, Eq. (5) becomes

$$\begin{aligned} \left. \frac{dq}{dT} \right|_p \equiv c_P &= \left(\frac{\partial u}{\partial T} \right)_v + \left[\left(\frac{\partial u}{\partial v} \right)_T + P \right] \left. \frac{dv}{dT} \right|_p \\ c_P &= c_V + \left[\left(\frac{\partial u}{\partial v} \right)_T + P \right] \left(\frac{\partial v}{\partial T} \right)_p = c_V + \left[\frac{a}{v^2} + P \right] \left(\frac{\partial v}{\partial T} \right)_p \text{ since } u = cT - a/v \end{aligned}$$

And from

$$\left(P + \frac{a}{v^2} \right) (v - b) = RT$$

Then

$$\left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{P + \frac{a}{v^2} - \frac{2a(v-b)}{v^3}}$$

Then

$$C_P - C_V = \left[\frac{a}{v^2} + P \right] \left(\frac{\partial v}{\partial T} \right)_p = \left[\frac{\frac{a}{v^2} + P}{P + \frac{a}{v^2} - \frac{2a(v-b)}{v^3}} \right] R$$

CHAPTER 5

Ideal Gas

5.1: EQUATION OF STATE OF A GAS

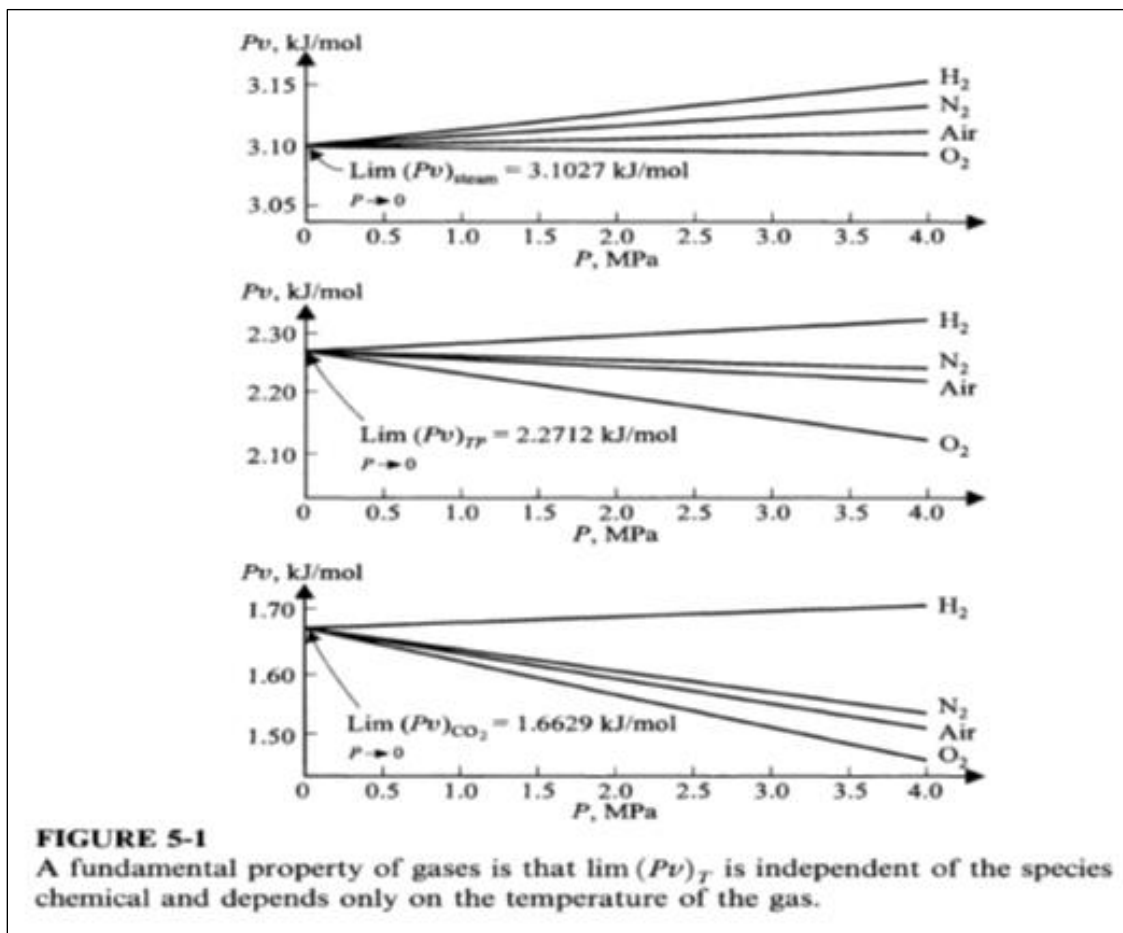
Let P is the pressure of an ideal gas and $v = V/n$ is the specific volume of *a real gas*. Experiments show that

$$Pv = A(1 + BP + CP^2 + \dots) \dots \dots (5 \cdot 1)$$

Where $A, B, C, \text{etc.}$, are *virial coefficients* which depend on the temperature and on the nature of the gas.

It was found experimentally that as the pressure approach zero, the product Pv approach a constant value A that depend only on the temperature and independent on the nature of a gas;

$$\lim_{P \rightarrow 0} (Pv) = A = \begin{cases} \text{function of temperature only,} \\ \text{independent of gas.} \end{cases} \quad (5.2)$$



The ideal gas temperature is defined in chapter 1 as;

$$T = 273.16 \text{ K} \lim_{P_3 \rightarrow 0} \left(\frac{P}{P_3} \right) \cdots (\text{constant } V) \quad (5.3)$$

so that
$$T = 273.16 \text{ K} \lim \frac{PV/n}{P_{TP}V/n} = 273.16 \text{ K} \frac{\lim (Pv)}{\lim (Pv)_{TP}},$$

and
$$\lim (Pv) = \left[\frac{\lim (Pv)_{TP}}{273.16 \text{ K}} \right] T.$$

The bracketed term is called the *molar gas constant* and is denoted by R . Thus,

$$R = \frac{\lim (Pv)_{TP}}{273.16 \text{ K}} \quad (5.4)$$

The constant R is called the gas constant, where $R = 8.31 \text{ J/mol.K}$.

Finally, substituting in eq.(5.2) then,

$$\lim (PV) = nRT,$$

Which is the experimental equation of state of an ideal gas.

From eq. (5.4) it follow that

$$\lim (Pv) = A = R\bar{T},$$

Then eq.(5.1) becomes

$$\frac{Pv}{RT} = 1 + BP + CP^2 + \cdots \quad (5.5)$$

5.1 INTERNAL ENERGY OF A REAL GAS

Internal energy of Free Expansion

In general, the internal energy of any gas is a function of any two of the coordinates P , V , and T .
So;

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \quad (5.6)$$

If $dT = 0$, and $dU = 0$ as the case of free expansion then

$$\left(\frac{\partial U}{\partial V} \right)_T = 0 \quad (5.7)$$

Which means that U is independent on V .

Now consider U is a function of P , and T , then

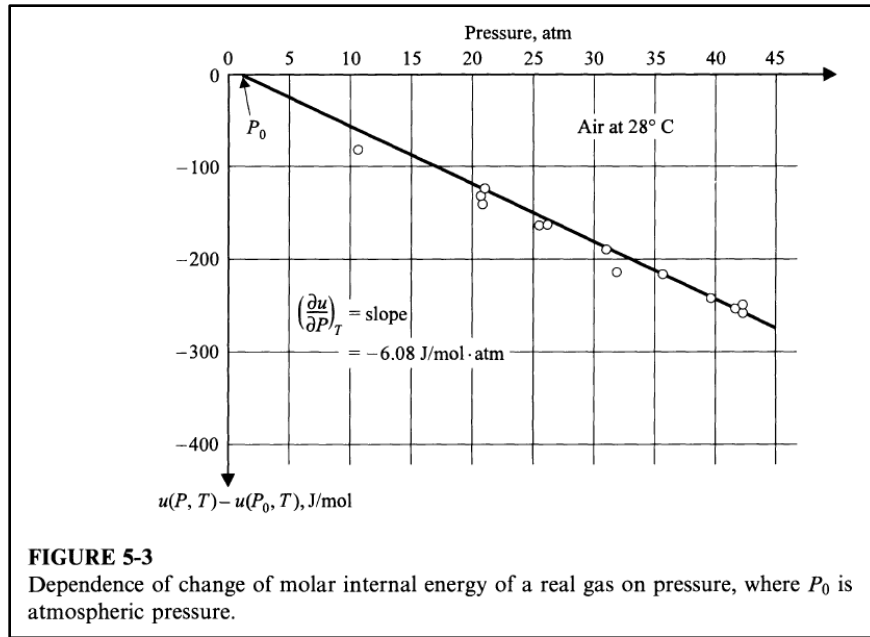
$$dU = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT \quad (5.8)$$

If $dT = 0$, and $dU = 0$ as the case of free expansion then

$$\left(\frac{\partial U}{\partial P}\right)_T = 0 \quad (5.9)$$

Which means that U is independent on P in the case of free expansion.

Experiments performed under *isothermal expansion* in which heat is transferred and work is done for measuring the quantity $(\partial u/\partial P)_T$, where u is the molar internal energy is shown in figure 5-2.



Rossini and Frandsen's with air, oxygen, and mixtures of oxygen and carbon led to the conclusion that the internal energy is a function of both temperature and pressure, They found no pressure or temperature range in which $(\partial u/\partial P)_T = 0$

5.3: IDEAL GAS

We have for a real gas only as the pressure approaches zero does the equation of state take the simple form

$$PV = nRT$$

Furthermore the internal energy is a function of P , and T ,

Then we can define the ideal gas is the gas whose properties approach the real gas properties at low pressure.

The ideal gas, then satisfy the following properties

$$\boxed{\begin{matrix} PV = nRT \\ \left(\frac{\partial U}{\partial P}\right)_T = 0 \end{matrix}} \quad (\text{ideal gas}). \quad (5.10)$$

Problem: given the following relation for ideal gas

$$\left(\frac{\partial U}{\partial P}\right)_T = 0$$

Proof that $U = U(T)$

Answer : To prove this we should prove first that $(\partial U/\partial V)_T = 0$

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T,$$

But

$$(\partial P/\partial V)_T = -nRT/V^2 = -P/V$$

Therefore

$$\left(\frac{\partial P}{\partial V}\right)_T \neq 0$$

But

$$\left(\frac{\partial U}{\partial P}\right)_T = 0$$

Then

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad (\text{ideal gas}) \dots\dots (5 \cdot 6)$$

Finally, since both $(\partial U/\partial P)_T = 0$ and $(\partial U/\partial V)_T = 0$, then

$$\boxed{U = f(T) \text{ only.} \quad (5.11)}$$

Now for infinitesimal quasi –static process of a hydrostatic system, the first law is

$$\delta Q = dU + P dV,$$

and the heat capacity at constant volume is given by

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V.$$

For ideal gas U is a function of T only ; therefore,

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{dU}{dT}$$

Then

$$\boxed{\delta Q = C_V dT + P dV.} \quad (5.12)$$

Now, all equilibrium states are represented by the ideal-gas equation,

$$PV = nRT,$$

and, for an infinitesimal quasi-static process,

$$P dV + V dP = nR dT.$$

Substituting the above in Eq. (5.8), we get

$$\delta Q = (C_V + nR)dT - V dP,$$

and dividing by dT yields

$$\frac{\delta Q}{dT} = C_V + nR - V \frac{dP}{dT}.$$

At constant P , this equation becomes

$$\left(\frac{dQ}{dT} \right)_p = C_v + nR$$

But $\left(\frac{dQ}{dT} \right)_p = C_p$, then

$$\boxed{C_p = C_V + nR} \quad (\text{ideal gas}). \quad (5.13)$$

Question Explain why for an ideal gas

$$C_p > C_v.$$

Answer

The reason is the following: As heat is supplied to a system at constant pressure, the gas expands and works against the external pressure, which, of course, is equal to the pressure of the gas in a quasi-static process. Thus, C_p includes work of expansion, which is not found in the constant volume ($\int P dV = 0$) heat capacity C_v .

Since U is a function of T only for an ideal gas, it follows that

$$C_v = \frac{dU}{dT} = \text{a function of } T \text{ alone,}$$

and so $C_p = C_v + nR = \text{a function of } T \text{ alone.}$

One more useful equation can be obtained. Since

$$dQ = (C_v + nR)dT - V dP,$$

we find $dQ = C_p dT - V dP.$ (5.14)

5.4 EXPERIMENTAL DETERMINATION OF HEAT CAPACITY

The heat capacities of real gases are measured by the electrical method. To measure C_v , the gas is contained in a thin-walled steel flask with a heating wire wound around it. By maintaining an electric current in the wire, an equivalent amount of heat is supplied to the gas, and the heat capacity at constant volume is obtained by measuring the temperature rise of the gas.

- (a) c_v is constant over a wide temperature range and is very nearly equal to $\frac{3}{2}R$.
- (b) c_p is constant over a wide temperature range and is very nearly equal to $\frac{5}{2}R$.
- (c) the ratio $c_p/c_v = \gamma$ is constant over a wide temperature range and is very nearly equal to $\frac{5}{3}$.

same method is used to measure C_p except that, instead of confining the gas to a constant volume, the gas is allowed to flow at constant pressure through a calorimeter, where it receives electrically a known equivalent heat per unit of time. From the initial (inlet) and final (outlet) temperatures, the rate of supply of heat, and the rate of flow of gas, the value of C_p is calculated.

3. *So-called permanent diatomic gases*, namely, air, H₂, D₂, O₂, N₂, NO, and CO:
- c_V is constant at ordinary temperatures, being equal to about $\frac{5}{2}R$, and increases as the temperature is raised.
 - c_P is constant at ordinary temperatures, being equal to about $\frac{7}{2}R$, and increases as the temperature is raised.
 - the ratio $c_P/c_V = \gamma$ is constant at ordinary temperatures, being equal to about $\frac{7}{5}$, and decreases as the temperature is raised.
4. *Polyatomic gases and gases that are chemically active*, such as CO₂, NH₃, CH₄, Cl₂, and Br₂:

c_P , c_V , and c_P/c_V vary with the temperature, the variation being different for each gas.

Monatomic	Rigid Diatomic	Vibrating Diatomic
$U = \frac{3}{2}nRT$	$U = \frac{5}{2}nRT$	$U = \frac{7}{2}nRT$
$C_V = \frac{3}{2}nR$	$C_V = \frac{5}{2}nR$	$C_V = \frac{7}{2}nR$
$C_P = \frac{5}{2}nR$	$C_P = \frac{7}{2}nR$	$C_P = \frac{9}{2}nR$
$\gamma = \frac{C_P}{C_V} = \frac{5}{3}$	$\gamma = \frac{C_P}{C_V} = \frac{7}{5}$	$\gamma = \frac{C_P}{C_V} = \frac{9}{7}$
Internal energy due to 3 translational DoF . s = 3	Internal energy due to 3 translational DoF plus 2 rotational DoF. s = 5	Internal energy due to 3 translational DoF plus 2 Rotational DoF plus 2 Vibrational DoF. s = 7

5.5 QUASI-STATIC ADIABATIC PROCESS

$$dQ = C_V dT + P dV,$$

and

$$dQ = C_P dT - V dP.$$

In an adiabatic process, $dQ = 0$, so

$$V dP = C_P dT,$$

and

$$P dV = -C_V dT.$$

Dividing the first equation by the second, we obtain

$$\frac{dP}{P} = -\frac{C_P}{C_V} \frac{dV}{V},$$

and denoting the ratio of the heat capacities by the symbol γ , we have

$$\frac{dP}{P} = -\gamma \frac{dV}{V}.$$

$$\ln P = -\gamma \ln V + \ln \text{const.},$$

or

$$\boxed{PV^\gamma = \text{const.}} \quad (5.15)$$

A family of curves representing quasi-static adiabatic processes may be plotted on a PV diagram by assigning different values to the constant in Eq. (5.11). The slope of any adiabatic curve is

$$\left(\frac{\partial P}{\partial V}\right)_S = -\gamma \text{const. } V^{-\gamma-1}$$

or

$$\left(\frac{\partial P}{\partial V}\right)_S = -\gamma \frac{P}{V}, \quad (5.16)$$

where the subscript S is used to denote a reversible adiabatic process.

Quasi-static isothermal processes are represented by a family of equilateral hyperbolas obtained by assigning different values to T in the equation $PV = nRT$. Since

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{P}{V}, \quad (5.17)$$

Then we have

$$\left(\frac{\partial P}{\partial V}\right)_S / \left(\frac{\partial P}{\partial V}\right)_T = \gamma \quad (5.18)$$

Because $\gamma > 1$ then, the adiabatic curve has a steeper negative slope than isothermal curve at the same point. Look figure 5-5.

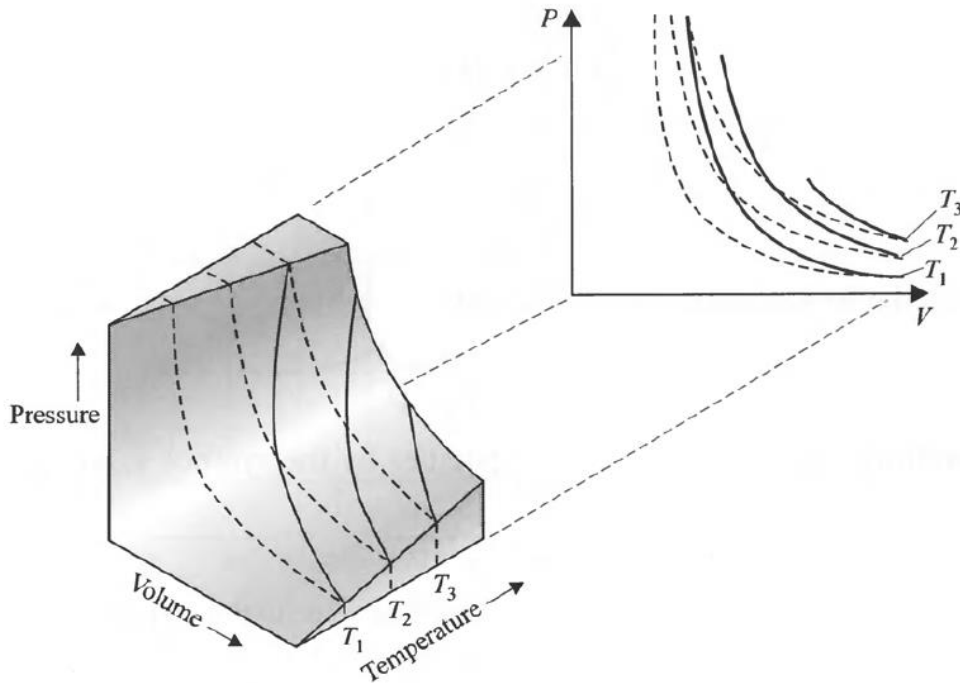


FIGURE 5-5

The PVT surface for the ideal gas and its projection onto a PV diagram. (Isotherms are shown as dashed curves, and adiabats as full curves.)

Problems

Problem 1 (5.9)

Prove that the work done *by* an ideal gas with constant heat capacities during a quasi-static adiabatic expansion is equal to:

$$(a) \quad W = -C_V(T_i - T_f).$$

$$(b) \quad W = \frac{P_f V_f - P_i V_i}{\gamma - 1}.$$

Answer

(a) The first law of thermodynamic is

$$\Delta U = Q + W$$

For adiabatic process $Q = 0$, so

$$\Delta U = W$$

but

$$\Delta U = C_V \Delta T$$

Then

$$W = C_V \Delta T = C_V (T_f - T_i) = -C_V (T_i - T_f)$$

(b)

$$dW = -PdV$$

$$PV^\gamma = C$$

$$dW = -CV^{-\gamma} dV$$

$$W = - \int_i^f CV^{-\gamma} dV$$

$$W = - \frac{CV^{\gamma+1}}{1-\gamma} \Big|_{V_i}^{V_f} = - \frac{CV_f^{-\gamma+1} - CV_i^{-\gamma+1}}{1-\gamma} = - \frac{P_f V_f^\gamma V_f^{-\gamma+1} - P_i V_i^\gamma V_i^{-\gamma+1}}{1-\gamma}$$
$$W = - \frac{P_f V_f - P_i V_i}{1-\gamma} = \frac{P_f V_f - P_i V_i}{\gamma - 1}$$

CHAPTER 6

The Second Law of Thermodynamics

6.1 : CONVERSION OF WORK INTO HEAT AND VICE VERSA

The first law of thermodynamics tells us that, in any process, energy is conserved. It may be converted from one form to another but the total amount of energy is unchanged. The second law of thermodynamics imposes limits on the *efficiency* of processes which convert heat into work, such as system or internal combustion engines.

Although we know that work may be converted into heat by a suitable dissipative mechanism (Joule's paddle wheels, or a resistor), we have not examined the conversion of heat into work. The first law emphasized *the equivalence* of heat and work as forms of energy, but it tells us nothing about the conversion from one form to the other; and, in particular, it tells us nothing about the *efficiency* with which heat may be converted into work, a matter of enormous practical importance.

To convert heat into work, we must also have at hand a process, by means of which such a conversion may continue indefinitely without any changes in the state of the system. What we need is a series of processes in which a system is brought back to its initial state (cycle).

Each of the processes that constitute the cycle involves either the performance of work or a flow of heat between the system and its surroundings, which consist of higher temperature reservoir and lower temperature reservoir

Let

- *The symbol $|Q_H|$ represent the heat exchanged between the high-temperature reservoir and the system*
- *The symbol $|Q_L|$ represent the heat exchanged between the low-temperature reservoir and the system*
- *The symbol $|W|$ represent the work exchanged between the system and the surrounding*

All the three $|Q_H|$, $|Q_L|$, and $|W|$ are expressed as *absolute values*, that is *positive values*. If $|Q_H|$ is larger than $|Q_L|$ and if $|W|$ is done by the system, the mechanical device by whose agency the system is caused to undergo the cycle is called *a heat engine*.

The heat engine: is a machine that absorbs a heat $|Q_H|$ from hot reservoir. turns part from this heat into work and the other part $|Q_L|$ is rejected to the cold reservoir.

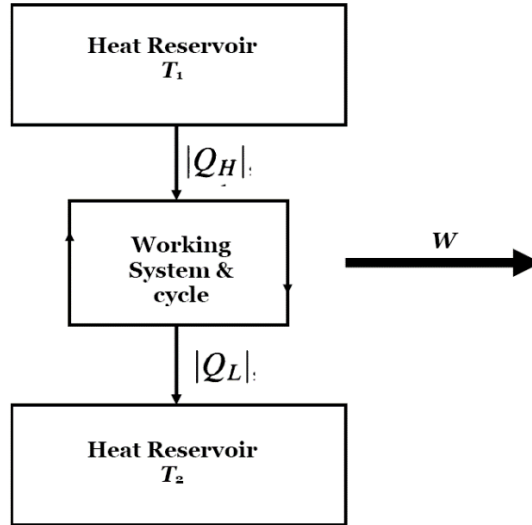


Figure 5-1: Diagram of heat engine

eg.

STEAM ENGINE Superheated steam in. Condensed water out

PETROL ENGINE Hot ignited petrol vapour+ air in Cooler exhaust gases out

i) Efficiency of a Heat Engine.

$$\text{Thermal efficiency} = \frac{\text{Work out}}{\text{heat input}}$$

or

$$\eta = \frac{|W|}{|Q_H|}, \quad (6.1)$$

Where $|Q_H|$ and $|W|$ are measured in joules. Applying the first law to one complete cycle, remembering that there is no change of internal energy, we get

$$|Q_H| - |Q_L| = |W|,$$

and, therefore,

$$\eta = \frac{|Q_H| - |Q_L|}{|Q_H|},$$

or

$$\eta = 1 - \frac{|Q_L|}{|Q_H|} \quad (6.2)$$

Note: Thermal efficiency will be 100% only if $|Q_L|=0$. We shall see later under what conditions this is possible in principle and why it is not possible in practice.

There are two types of engine:

- External combustion engine (such as the Stirling engine and the steam engine)
- Internal-combustion engine (such as the gasoline engine and the diesel engine.)

In both types, a gas or a mixture of gases contained in a cylinder undergoes a cycle, thereby causing a piston to impart to a shaft a motion of rotation against an opposing force.

6.2 The Stirling engine

In 1816 a minister of the Church of Scotland named Robert Stirling designed and patented a hot-air engine that could convert some of the energy liberated by a burning fuel into work. The steps in the operation of a somewhat idealized Stirling engine are shown schematically in Fig. 2-1 a.

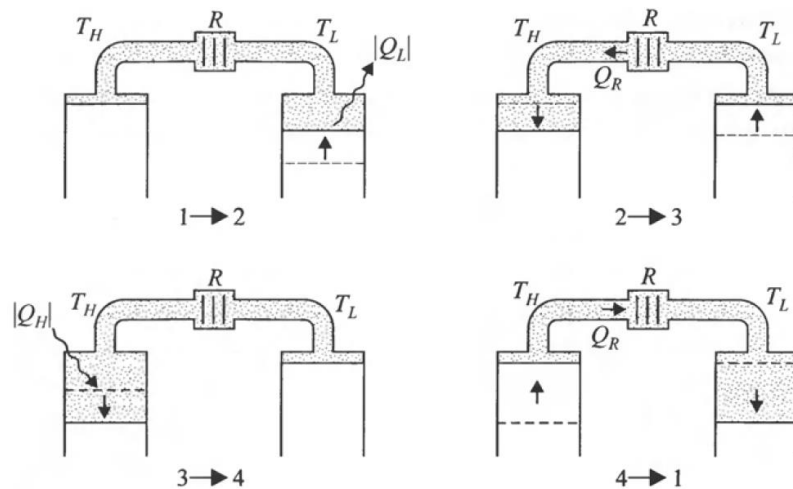


Figure 2 : (a) Schematic diagram of steps in the operation of an idealized Stirling engine.

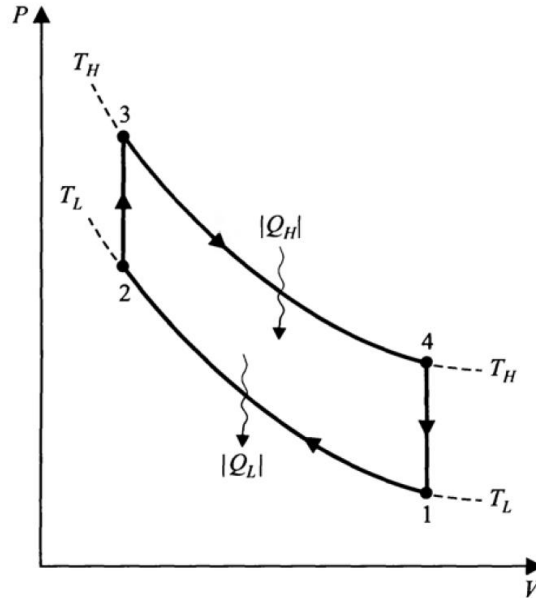


Fig. 6-2 b: The numbers under each diagram refer to the processes shown on PV diagram

Two pistons, an expansion piston on the left and a compression piston on the right, are connected to the same shaft. As the shaft rotates, these pistons move in different phase, with the aid of suitable connecting linkages. The space between the two pistons is filled with gas, and the left-hand portion of the space is kept in contact with a hot reservoir (burning fuel), while the right-hand portion is in contact with a cold reservoir. Between the two portions of gas is a device R, called a regenerator, consisting of a packing of steel wool or a series of metal baffles, whose thermal conductivity is low enough to support the temperature difference between the hot and cold ends without appreciable heat conduction.

The Stirling cycle consists of four processes depicted schematically in Fig. 6-2 b and involving pressure and volume changes plotted (as though ideal conditions existed) on the PV diagram of Fig. 6-2 b.

1—2 While the left piston remains at the top, the right piston moves halfway up, compressing cold gas while in contact with the cold reservoir and therefore causing heat Q_c to leave. This is an approximately isothermal compression and is depicted as a rigorously isothermal process at the temperature θ_c in Fig. 6-2b.

2—3 The left piston moves down and the right piston up, so that there is no change in volume, but gas is forced through the regenerator from the cold side to the hot side and enters the left-hand side at the higher temperature θ_H . To accomplish this, the regenerator supplied heat Q_r to the gas. Note that the process 2 —3 in Fig. 6-2 b is at constant volume.

3 → 4 The right piston now remains stationary as the left piston continues moving down while in contact with the hot reservoir, causing the gas to undergo an approximately isothermal expansion, during which heat Q_H is absorbed at the temperature, as shown in Fig. 6-2 b.

The, net result of the cycle is the absorption of heat $|Q_H|$ at the high temperature T_H , the rejection of heat $|Q_L|$ at the low temperature T_L , and the delivery of work $W = |Q_H| - |Q_L|$ to the surroundings, with no net heat transfer resulting from the two constant-volume processes.

The Stirling engine has some unique advantages compared with other heat engines.

- 1- The engine can use any heat source (heating from radioactivity to combustion of biomass waste products)
- 2- Using open -air combustion
- 3- The engine does not produce toxic exhaust

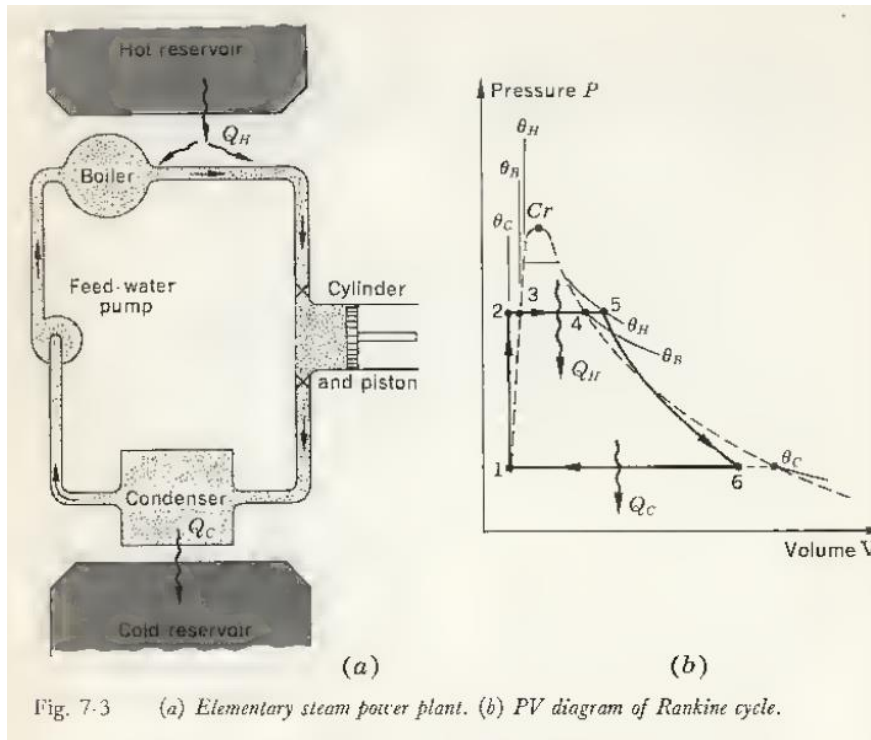
Applications

- 1- An interesting application is an implantable Stirling engine for artificial heart power, which is being developed at the Joint Center for Graduate Study, University of Washington.

6.3 STEAM ENGINE

The steam is historically quite important, because it was the first engine driven by heat, rather than animals, water, or wind.

A schematic diagram of an elementary steam power plant is shown in Fig. 6-3a.



6-4: INTERNAL COMBUSTION ENGINE

- Gasoline Engine

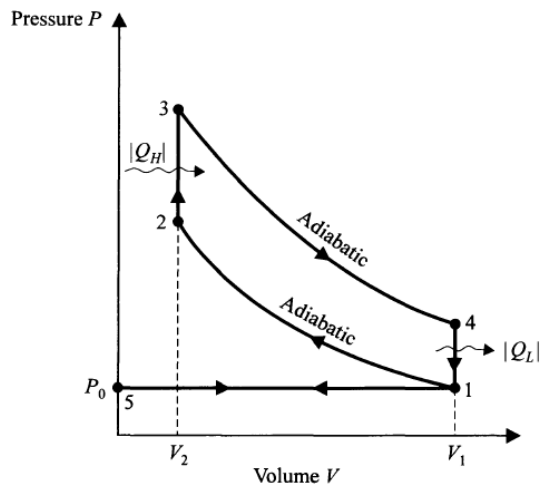


Figure 6.4: Otto Cycle for idealized gasoline engine.

- (1) The behavior of a gasoline engine can be approximated by assuming a set of ideal conditions
- (2) All processes are quasi-static.

(3) There is no friction.

On the basis of these assumptions the standard Otto cycle is composed of six simple processes of an ideal gas four of which require motion of the piston and are called *strokes* , (See Fig. 6-4a).

5 → 1 represents a quasi-static isobaric intake at atmospheric pressure. There is no friction and no acceleration. The volume varies from zero to V_1 as the number of moles varies from zero to n according to the equation

$$P_0V = nRT_1,$$

where P_0 is atmospheric pressure and T_1 is the temperature of the outside air.

1 → 2 represents a quasi-static, *adiabatic* compression of n moles of air. There is no friction and no loss of heat through the cylinder wall. The temperature rises from T_1 to T_2 according to the equation

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1},$$

2 — 3 represents a quasi-static *isochoric* increase of temperature and pressure of n moles of air, brought about by an absorption of heat $|Q_H|$ from a series of external reservoirs whose temperatures range from T_2 to T_3 . If there were only one reservoir at temperature 3, the flow of heat would not be quasi-static. This process is meant to approximate the effect of the explosion in a gasoline engine.

3 —4 represents a quasi-static adiabatic expansion of n moles of air, involving a drop in temperature from T_3 to T_4 according to the equation

$$T_3V_2^{\gamma-1} = T_4V_1^{\gamma-1},$$

4 —1 represents a quasi-static isochoric drop in temperature and pressure of n moles of air, brought about by a rejection of $|Q_c|$ heat to a series of external reservoirs ranging in temperature from T_4 to T_1 . This process is meant to approximate the drop to atmospheric pressure upon opening the exhaust valve.

1 —5 represents a quasi-static isobaric exhaust at atmospheric pressure. The volume varies from V_1 to zero as the number of moles varies from n to zero, with the temperature remaining constant at the value T_1 .

Note: The two isobaric processes 5 → 1 and 1 → 5 obviously cancel each other

- **Summary of Otto cycle for gasoline engine:**

The Otto cycle consists of two constant -volume steps during which heat is transferred, connected by two adiabatic, as shown in the figure.

$$\begin{aligned}
 \text{Step1} \rightarrow 2: \quad Q_{12} &= 0 & W_{12} &= \Delta U_{12} = C_V(T_2 - T_1) \\
 \text{Step2} \rightarrow 3: \quad W_{23} &= 0 & Q_{23} &= Q_H = \Delta U_{23} = C_V(T_3 - T_2) \\
 \text{Step3} \rightarrow 4: \quad Q_{34} &= 0 & W_{34} &= \Delta U_{34} = C_V(T_4 - T_3) \\
 \text{Step4} \rightarrow 1: \quad W_{41} &= 0 & Q_{41} &= Q_L = \Delta U_{41} = C_V(T_1 - T_4)
 \end{aligned}$$

$$\begin{aligned}
 \eta &= \frac{|W_{\text{cycle}}|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{C_V(T_4 - T_1)}{C_V(T_3 - T_2)} \\
 \eta &= 1 - \frac{(T_4 - T_1)}{(T_3 - T_2)} \dots \dots (6.3)
 \end{aligned}$$

The two adiabatic processes during the compression stroke and power stroke are given by

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1},$$

and

$$T_4 V_1^{\gamma-1} = T_3 V_2^{\gamma-1},$$

which yield, after division,

$$\frac{T_1}{T_4} = \frac{T_2}{T_3}.$$

Change signs and add unity to obtain

$$\frac{T_4 - T_1}{T_4} = \frac{T_3 - T_2}{T_3},$$

or

$$\frac{T_4 - T_1}{T_3 - T_2} = \frac{T_4}{T_3}.$$

Combine this result with Eq. (6.4) and Eq. (6.3) to obtain the thermal efficiency η of an idealized gasoline engine,

$$\eta = 1 - \frac{T_1}{T_2}, \tag{6.5}$$

It shows that the thermal efficiency of a gasoline engine working in the Otto cycle depends on the temperature before and after compression. In a gasoline engine with temperatures $T_1 = 300 \text{ K}$ and $T_2 = 580 \text{ K}$, the efficiency is 48 percent.

This is the optimum efficiency for a gasoline engine operating in an idealized quasi-static Otto cycle for the temperatures cited.

6.3 THE DIESEL ENGINE

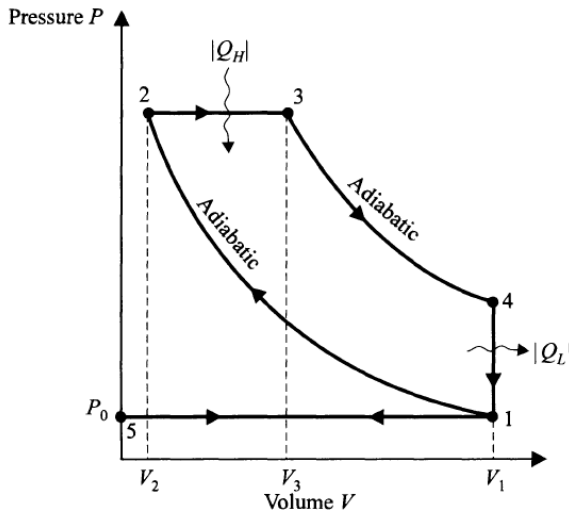


FIGURE 6-2
Idealized Diesel cycle for oil-fired engines shown on a PV diagram.

- In comparison to gasoline engine, the process $2 \rightarrow 3$ of an air-standard diesel engine is an isobaric heat absorption while the volume expands quasi-statically
- $2 \rightarrow 3$ is a vertical line in Otto's while it's a horizontal line in Diesel's.

$$\eta = 1 - \frac{1}{\gamma} \frac{(r_E^\gamma - 1)}{(r_E - 1)} \cdot \frac{T_1}{T_2}, \quad (6.6)$$

where the *expansion ratio* r_E (also called the “cutoff ratio” in engineering) is given by

$$r_E = \frac{V_1}{V_3}$$

and T_1 and T_2 are the temperatures at the beginning and end of the compression stroke, respectively. Interestingly, the efficiency of the Diesel cycle expressed in Eq. (6.6) does not depend on the *compression ratio* r_C given by

$$r_C = \frac{V_1}{V_2}.$$

Taking, for example, $r_E = 5$, $\gamma = 1.4$, $T_1 = 300$ K, and $T_2 = 990$ K, we obtain

$$\begin{aligned} \eta &= 1 - \frac{(5^{1.4} - 1)}{(1.4)(5 - 1)} \cdot \frac{300 \text{ K}}{990 \text{ K}} \\ &= 54 \text{ percent.} \end{aligned}$$

6-5 HEAT ENGINE:KELVIN -BLANCK STATEMENT OF THE SECOND LAW

Thermodynamics owes its origin to the attempt of *conversion of heat into work* and to develop the theory of operation of devices for this purpose. It is therefore fitting that one of the fundamental laws of thermodynamics is based upon the operation of heat engines.

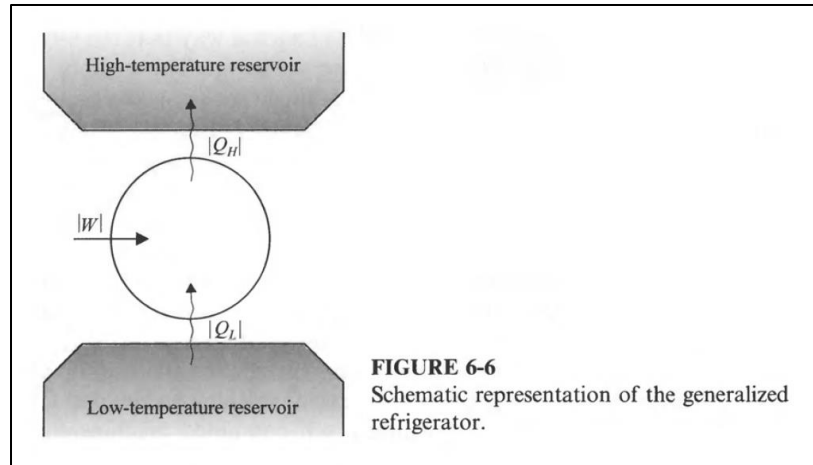
The second law originated as an empirical statement about the limitations of heat engines. There are two early statements of the second law made after empirical observation of how the real world behaved

- i) **The Kelvin-Planck Statement:** “*No process is possible whose sole result is the absorption of heat from a reservoir and the conversion of this heat into work.*”.

6-7: REFREGIRATOR; CLAUSIUS STATEMENT OF THE SECOND LAW

We have seen that a **heat engine is:** a device by which a system is taken through a cycle in such a direction that some heat is absorbed at high temperature, a smaller amount is rejected at a lower temperature, and a net amount of work is done *by* the system on the outside.

Refrigerator: is a device work in the opposite direction to that of an engine : the absorption of some heat at a low temperature, the rejection of *a larger* amount at higher temperature, and a net amount of work done *on* the system, as shown in figure 6-6.



The Stirling cycle is capable of being reversed and, when reversed, it gives rise to one of the most useful types of refrigerator.

Figure 6-6 represents a schematic diagram of a refrigerator.

Let the following notation (all positive quantities) refer to one complete cycle:

$|Q_H|$ represents the amount of heat rejected by the refrigerant to the high-temperature reservoir;

$|Q_L|$ represents the amount of heat absorbed by the refrigerant from the low-temperature reservoir; and

$|W|$ represents the net work done on the refrigerant by the surroundings.

Since the refrigerant undergoes a cycle, there is no change in internal energy, and the first law becomes

$$|Q_L| - |Q_H| = |W|,$$

or

$$|Q_H| = |Q_L| + |W|.$$

Efficiency of the refrigerator : From the definition efficiency of refrigerator is given by

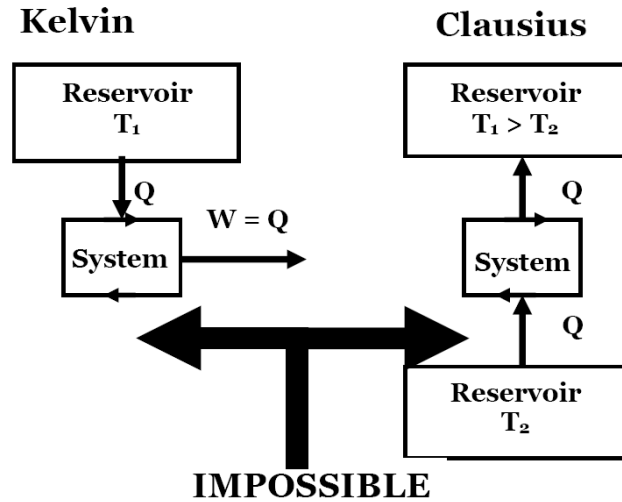
$$\eta = \frac{|Q_L|}{|W|} = \frac{|Q_L|}{|Q_H| - |Q_L|}$$

Work is always necessary to transfer heat from a lower-temperature reservoir to a higher temperature reservoir, this because the nature fact is that heat does not flow spontaneously from a lower-temperature reservoir to a higher temperature reservoir. This negative statement leads to the *Clausius statement of the second law*.

“No process is possible whose sole result is the transfer of heat from a cooler to a hotter body.”

6-8: EQUIVALENCE OF KELVIN-PLANCK AND CLAUSIUS STATEMENTS

At first sight, the Kelvin-Planck and the Clausius statements appear to be quite unconnected, but we shall see immediately that they are in all respects equivalent.

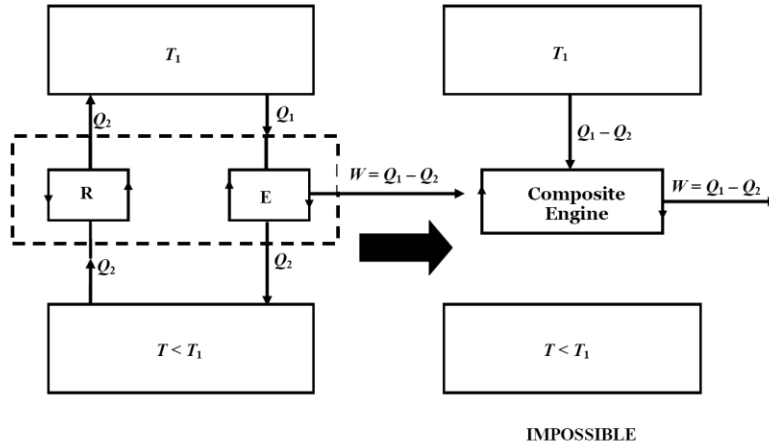


Two statements are said to be equivalent in two ways:

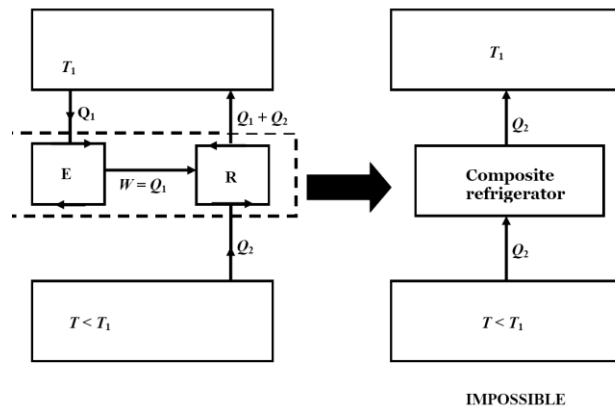
- 1- The truth of one implies the truth of the second and the truth of the second implies the truth of the first.
- 2- The violation of one implies the violation of the second, and violation of the second implies the violation of the first.

We will select the second way (we will prove The violation of Kelvin-Planck statement implies the violation of Clausius statement , and violation of Clausius statement implies the violation of Kelvin-Planck statement).

To prove that violation of Clausius statement implies the violation of Kelvin-Planck, consider a refrigerator, shown in the left-hand side of P'ig. 7-10, which requires no work to transfer Q_2 units of heat from a cold reservoir to a hot reservoir and which therefore violates the Clausius statement. Suppose that a heat engine (on the right) also operates between the same two reservoirs in such a way that heat Q_2 is delivered to the cold reservoir. The engine, of course, does not violate any law, but the refrigerator and engine together constitute a self-acting device whose sole effect is to take heat $Q_1 - Q_2$ from the hot reservoir and to convert all this heat into work. Therefore the refrigerator and engine together constitute a violation of the Kelvin-Planck statement.



Now, to prove that violation of Kelvin-Planck statement implies the violation of Clausius statements consider an engine, shown on the left hand side of Fig. 6-11, which rejects no heat to the cold reservoir and which therefore violates the Kelvin-Planck statement. Suppose that a refrigerator (on the right) also operates between the same two reservoirs and uses up all the work liberated by the engine. The refrigerator violates no law, but the engine and refrigerator *together* constitute a self-acting device whose sole effect is to transfer heat Q_2 from the cold to the hot reservoir. Therefore the engine and refrigerator together constitute, a violation of the Clausius statement.



Problems

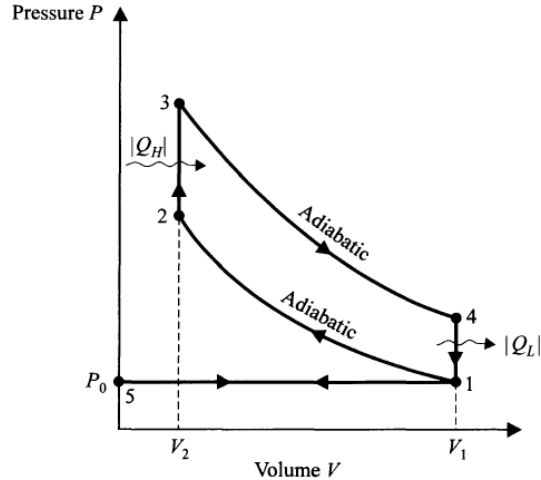
6.1. Show that the thermal efficiency of an ideal Otto cycle is given by

$$\eta = 1 - \frac{1}{r^{\gamma-1}}$$

Where the ratio $r = V_1/V_2$ is called either the compression ratio or the expansion ratio. of the spark. Calculate η when $r = 9$ and $\gamma = 1.5$

Solution

The Otto cycle consists of 4-steps: two constant -volume steps during which heat is transferred, connected by two adiabatic, as shown in the figure.



$$\begin{aligned}
 \text{Step 1} \rightarrow 2: \quad Q_{12} &= 0 & W_{12} &= \Delta U_{12} = C_V(T_2 - T_1) \\
 \text{Step 2} \rightarrow 3: \quad W_{23} &= 0 & Q_{23} &= Q_H = \Delta U_{23} = C_V(T_3 - T_2) \\
 \text{Step 3} \rightarrow 4: \quad Q_{34} &= 0 & W_{34} &= \Delta U_{34} = C_V(T_4 - T_3) \\
 \text{Step 4} \rightarrow 1: \quad W_{41} &= 0 & Q_{41} &= Q_L = \Delta U_{41} = C_V(T_1 - T_4)
 \end{aligned}$$

$$\begin{aligned}
 \eta &= \frac{|W_{\text{cycle}}|}{|Q_H|} = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|} \\
 &= 1 - \frac{C_V(T_4 - T_1)}{C_V(T_3 - T_2)} = 1 - \frac{(T_4 - T_1)}{(T_3 - T_2)} \dots (1)
 \end{aligned}$$

The two adiabatic process during the compression and power stroke satisfy the following relations:

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \dots (2)$$

$$T_4 V_1^{\gamma-1} = T_3 V_2^{\gamma-1} \dots (3)$$

Which yield after division

$$\frac{T_1}{T_4} = \frac{T_2}{T_3} \dots (4)$$

Changing sign and adding unity to obtain

$$\frac{T_4 - T_1}{T_4} = \frac{T_3 - T_2}{T_3}$$

Or

$$\frac{T_4 - T_1}{T_3 - T_2} = \frac{T_4}{T_3}$$

Combining this result with Eq. (1) and Eq. (4) then

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

But from Eq.(2)

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1} = \frac{1}{\left(\frac{V_1}{V_2}\right)^{\gamma-1}}$$

Then

$$\eta = 1 - \frac{1}{\left(\frac{V_1}{V_2}\right)^{\gamma-1}} = 1 - \frac{1}{r^{\gamma-1}}, \quad \text{where } r = \frac{V_1}{V_2}$$

When $r = 9$ and $\gamma = 1.5$, then

$$\eta = 1 - \frac{1}{\sqrt{9}} = 0.67 = 67\%$$

CHAPTER 7

The Carnot Cycle and the Thermodynamic Temperature Scale

7-1: CARNOT CYCLE

Inasmuch as 100 percent efficiency is not allowed by the second law, let us ask the following questions:

- (1) What is the maximum efficiency that can be achieved by an engine operating between these two reservoirs?
- (2) What are the characteristics of such an engine?
- (3) Of what effect is the nature of the substance undergoing the cycle?

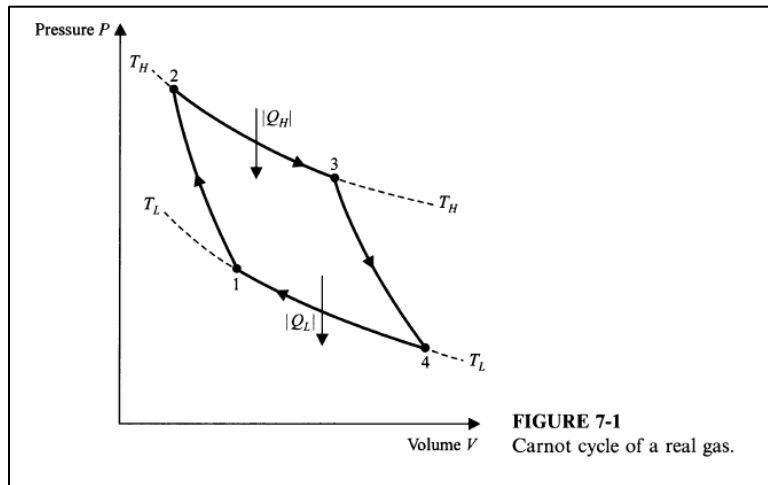
The importance of these questions was recognized by Nicolas Leonard Sadi Carnot who in the year 1824, before the first law of thermodynamics was firmly established, published a paper entitled "Reflections on the Motive power of Fire". In this paper Carnot described an ideal engine operating in a particularly simple cycle known today as the Carnot cycle.

An engine operating in a Carnot cycle is called a Carnot engine. A Carnot engine operates between two reservoirs in a particularly simple way. *All the heat that is absorbed is absorbed at a constant high temperature, namely, that of the hot reservoir. Also, all the heat that is rejected is rejected at a constant lower temperature, that of the cold reservoir.* Since all four processes are reversible, the Carnot cycle

is a reversible cycle.

7-2: EXAMPLES OF CARNOT ENGINE

Figure 7-1 shows the simplest example of Carnot cycle. The gas is not necessarily an ideal gas.



The dashed line marked T_H and T_L are isothermal curves. The gas is initially in the state represented by the point 1. The four processes are then:

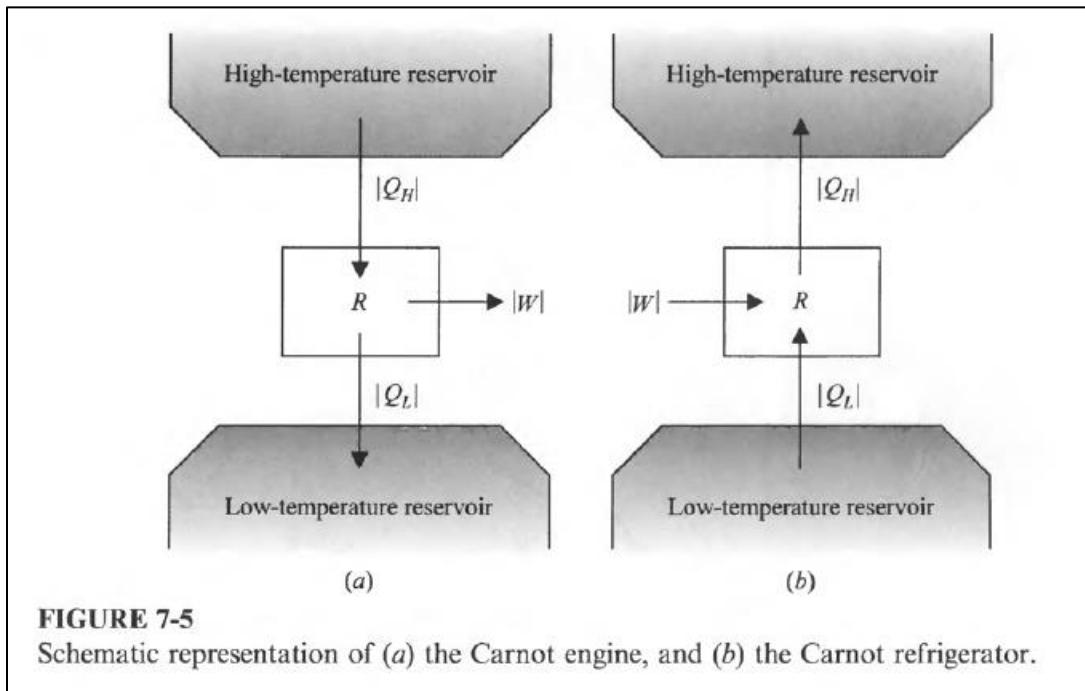
1. Process 1 \rightarrow 2: Reversible adiabatic compression until temperature rises to T_H
2. Process 2 \rightarrow 3: reversible isothermal expansion until the point 3 is reached.
3. Process 3 \rightarrow 4: Reversible adiabatic expansion until temperature drops to T_L .

4. Process 4 → 1: reversible isothermal compression until the original state reached.

During the isothermal expansion 2 → 3, heat $|Q_H|$ is absorbed from the hotter reservoir at T_H . During the isothermal compression 4 → 1, heat $|Q_L|$ is rejected to the cooler reservoir at T_L .

7-3: CARNOT REFRIGERATOR

Because Carnot cycle is reversible, then the reverse of Carnot engine is Carnot refrigerator. The figure 7-5 shows representation of Carnot refrigerator.



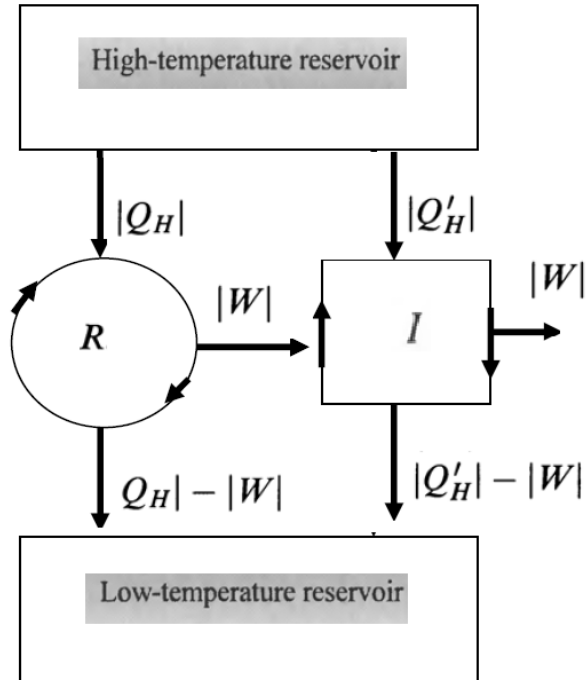
The importance of Carnot refrigerator is the same quantities of Carnot engine is used in Carnot refrigerator with the opposite sign.

7-4: CARNOT THEOREM AND COROLLARY

Carnot theorem states that “*No heat engine operating between two given reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs*”

Proof:

As shown in Figure - , imagine a Carnot engine R, which is *reversible*, and other engine I, which is *irreversible*, working between the same two reservoirs and adjust so that they both deliver the same amount of work $|W|$.



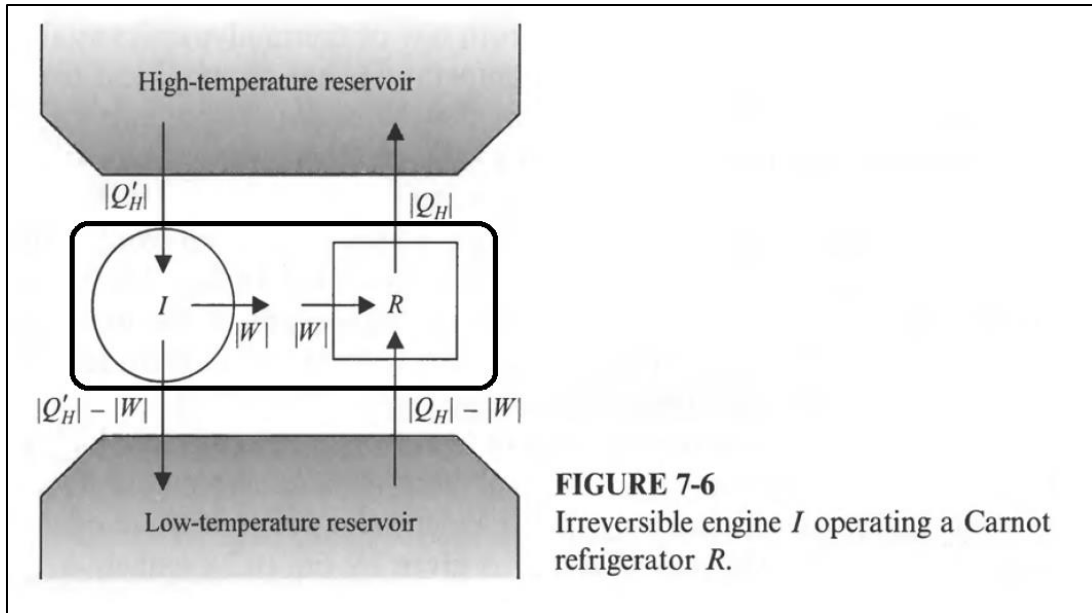
Let *us assume* that the efficiency of the engine *I* is greater than that of *R*;

$$\eta_I > \eta_R$$

$$\text{Or } \frac{|W|}{|Q_H|} > \frac{|W|}{|Q'_H|}$$

$$\text{So } |Q'_H| > |Q_H|$$

\Now let the engine *I* drive the Carnot engine an Carnot refrigerator. This is shown in figure 7-6



The net heat extracted from the low-temperature reservoir by the composite system

$$(|Q_H| - |W|) - (|Q'_H| - |W|) = |Q_H| - |Q'_H|,$$

The net heat delivered to the high-temperature reservoir is also

$$|Q_H| - |Q'_H|$$

The net heat extracted = The net heat delivered

the composite system transfer $|Q_H| - |Q'_H|$ from the cold and delivers the same amount of heat to the hot reservoir without work being done by the surroundings. This composite system violates the second law of thermodynamics (Clausius statement).

Then the assumption of $\eta_I > \eta_R$ is false and this proves Carnot theorem.

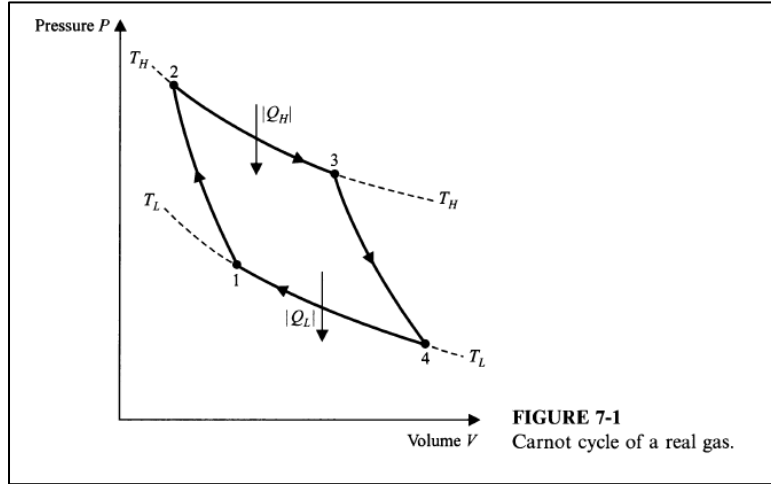
We may express this result in symbols, thus:

$$\eta_I \leq \eta_R \dots\dots (7.1)$$

A corollary to this theorem is that ***“all Carnot engines running between the same two reservoirs have the same efficiency”***.

Problem 4.5. Prove directly (by calculating the heat taken in and the heat expelled) that a Carnot engine using an ideal gas as the working substance has an efficiency of $1 - T_c/T_H$.

Answer:



As shown in figure 7-1, to compute $|Q_L|$ and $|Q_H|$, we need only to consider the isothermal

The isothermal process $2 \rightarrow 3$

For any infinitesimal reversible process of an ideal gas, the first law of thermodynamic can be written as;

$$dQ = C_V dT + PdV$$

Applying this equation to the isothermal process $2 \rightarrow 3$, the heat absorbed is

$$\begin{aligned} |Q_H| &= \int_{V_2}^{V_3} PdV \\ &= nRT_L \ln \frac{V_3}{V_2} \end{aligned}$$

Similarly, for the isothermal process $4 \rightarrow 1$

$$|Q_L| = nRT_H \ln \frac{V_4}{V_1}$$

Therefore

$$\frac{|Q_H|}{|Q_L|} = \frac{\ln \frac{V_3}{V_2}}{\ln \frac{V_4}{V_1}} \dots \dots (7.2)$$

Since the process $1 \rightarrow 2$ is adiabatic, we may write, for any infinitesimal portion

$$-C_V dT = PdV.$$

Or

$$-C_V dT = \frac{nRT}{V} dV$$

Integrating from $1 \rightarrow 2$, we get

$$\frac{1}{nR} \int_{T_L}^{T_H} C_V \frac{dT}{T} = \ln \frac{V_2}{V_1}$$

Similarly, for the adiabatic process $3 \rightarrow 4$,

$$\frac{1}{nR} \int_{T_H}^{T_L} C_V \frac{dT}{T} = \ln \frac{V_4}{V_3}$$

Therefore

$$\begin{aligned} \ln \frac{V_2}{V_1} &= \ln \frac{V_3}{V_4} \\ \text{or} & \dots\dots (7.3) \\ \ln \frac{V_3}{V_2} &= \ln \frac{V_4}{V_1} \end{aligned}$$

Combining eq.(7.2) and (7.3), we obtain

$$\frac{|Q_H|}{|Q_L|} = \frac{T_H}{T_L}$$

$$1 - T_L/T_H$$

$$\eta = 1 - \frac{T_L}{T_H}$$

CHAPTER 8

Entropy

We proved in chapter 7 , For Carnot engine that

$$\frac{|Q_H|}{|Q_L|} = \frac{T_H}{T_L}$$

$$\frac{Q_H}{Q_L} = -\frac{T_H}{T_L}$$

So actually, during this reversible process we have

$$\sum_n \left(\frac{Q_L}{T_L} + \frac{Q_H}{T_H} \right) = 0 \Rightarrow \oint \frac{dQ}{T} = 0 \quad (\text{reversible process})$$

Let us consider the following theorem stated by *Clausius*:

⇒ *"In an arbitrary cyclic process P, the following inequality holds:*

$$\oint_P \frac{dQ}{T} \leq 0$$

where the equality holds for P reversible."

2.4 Entropy

Since $\oint \frac{dQ}{T} = 0$ for reversible process, then $\frac{dQ}{T}$ is *exact differentia*. This implies that there a state function S called *entropy* whose differential is given as

$$dS = \frac{dQ}{T}$$

The entropy is defined up to an additive constant. The difference between entropies of any two states A and B is

$$S_A - S_B = \int_A^B \frac{dQ}{T}$$

What happens when the integration is along an irreversible path? Since I – R is a cycle (see **Fig. 2.5**), it follows from Clausius' theorem that

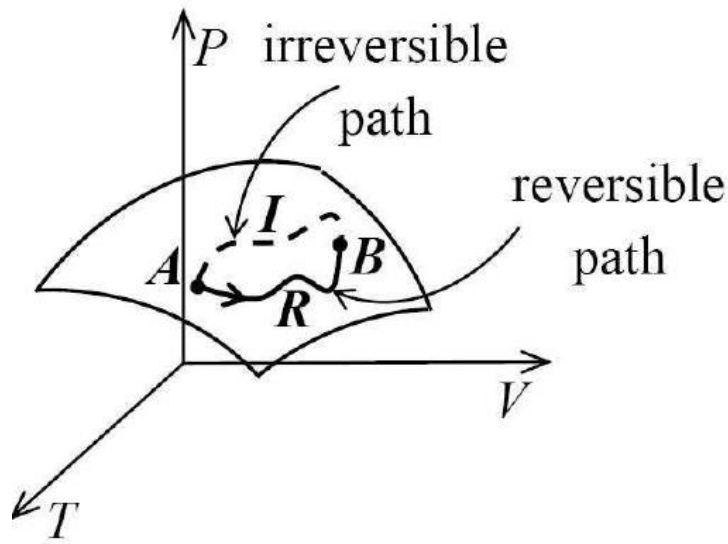


Figure 2.5: I – R (irreversible-reversible) cycle.

$$\oint_{I-R} \frac{\delta Q}{T} \leq 0 \Rightarrow$$

$$\Rightarrow \boxed{\int_I \frac{\delta Q}{T} \leq \int_R \frac{\delta Q}{T} = S(B) - S(A)}.$$

Therefore, in general

$$\boxed{\int_A^B \frac{\delta Q}{T} \leq S(B) - S(A)},$$

and the equality holds for a reversible process.

and the equality holds for a reversible process. In particular, for an isolated system, which does not exchange heat with a reservoir, $\delta Q = 0$ and therefore

$$\Delta S \geq 0.$$

This means that the entropy of an isolated system never decreases and remains constant during a reversible transformation.

Note:

i) The joint of a system and its environment is called "universe". Defined in this way, the "universe" is an isolated system and, therefore, its entropy never decreases. However, the entropy of a non-isolated system may decrease at the expense of the system's environment.

ii) Since the entropy is a state function, $S(B) - S(A)$ is independent of the path, regardless whether it is reversible or irreversible. For an irreversible path, the entropy of the environment changes, whereas for a reversible one it does not.

iii) Remember that the entropy difference

$$S_A - S_B = \int_A^B \frac{dQ}{T}$$

only when the path is reversible; otherwise the difference is larger than the integral

Example Problem (): The heat capacity at constant volume of a number of substances can be represented empirically by an equation of the form

$$C_V = a + bT + cT^2$$

where a , b , and c are constants. Calculate the change in internal energy and the change in entropy when the temperature changes from T_1 to T_2 at constant volume.

Solution

At constant volume, we have $dU = C_V dT$ and $\Delta U = \int_{T_1}^{T_2} C_V dT = \int_{T_1}^{T_2} (a + bT + cT^2) dT$.

Thus,

$$\Delta U = (aT + bT^2/2 + cT^3/3) \Big|_{T_1}^{T_2}$$

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} C_V/T dT = a \ln T + bT + cT^2/2 \Big|_{T_1}^{T_2}.$$

8.4 ENTROPY OF AN IDEAL GAS

If a system absorbs an infinitesimal amount of heat dQ_R during a reversible process, the entropy change of the system is equal to

$$dS = \frac{dQ_R}{T}$$

It is interesting to note that, although dQ_R , the ratio dQ_R/T is exact. The reciprocal of the absolute thermodynamic temperature is, therefore, the integrating factor of the integrating factor of dQ_R .

consider one of the expressions for dQ_R of an ideal gas,

$$dU = dQ + dW$$

$$dU = dQ - PdV$$

For reversible process

$$dS = \frac{dQ_R}{T}$$

Then

$$dQ_R = TdS$$

so

$$dU = TdS - PdV$$

For ideal gas we have

$$dU = C_V dT$$

So

$$C_V dT = TdS - PdV \dots (1)$$

Consequently

$$dS = C_V \frac{dT}{T} + \frac{P}{T} dV \dots (2)$$

But

$$PV = nRT$$

$$\frac{P}{T} = \frac{nR}{V}$$

Now in equation (2)

$$dS = C_V \frac{dT}{T} + \frac{nR}{V} dV$$

By integration this becomes

$$S_f = \int_i^f C_V \frac{dT}{T} + nR \ln \frac{V_f}{V_i} + S_i$$

$$\Delta S = \int_i^f C_V \frac{dT}{T} + nR \ln \frac{V_f}{V_i} \dots \dots (3)$$

- Calculate of ΔS in terms of C_p

we have

$$C_p = C_v + nR \dots (4)$$

And from the ideal gas law

$$PV = nRT$$

Then

$$PdV + VdP = nRdT$$

$$PdV = nRdT - VdP \dots (5)$$

From eq.(4) and eq. (5) with eq.(1),

Then

$$(C_p - nR)dT = TdS - nRdT - VdP$$

Which becomes

$$dS = C_p \frac{dT}{T} - \frac{VdP}{T} \dots (6)$$

And from the ideal gas law

$$PV = nRT$$

$$\frac{V}{T} = \frac{nR}{P}$$

Then eq. (6) becomes

$$dS = C_p \frac{dT}{T} - \frac{nRdP}{P}$$

With integration this becomes

$$\Delta S = \int_i^f C_p \frac{dT}{T} - nR \ln \int_i^f \frac{dP}{P}$$

$$\Delta S = \int_i^f C_P \frac{dT}{T} - nR \ln \frac{P_f}{P_i}$$

Or

$$\Delta S = \int_i^f C_P \frac{dT}{T} + nR \ln \frac{P_i}{P_f} \dots \dots (7)$$

Chapter 9:

Mathematical methods

9.1 : Characteristic function

Change of variables, known as *Legendre differential transformation*, yield functions that are fundamentally important in thermodynamics.

If the state of a system is described by a function of two variables $f(x, y)$, which satisfies the equation

$$df = udx + vdy \dots \dots (9.1)$$

and we wish to change the description to one involving a new function $g(u, y)$, satisfying a similar equation in terms of du and dy , then it is necessary to define the Legendre transform $g(u, y)$ as

$$g \equiv f - ux. \quad (9.2)$$

It is readily verified that g satisfies the equation

$$dg = -x du + v dy. \quad (9.3)$$

Let us apply this to the first law of thermodynamics.

Consider the first law of thermodynamics for a hydrostatic system with heat expressed in terms of temperature and entropy, namely,

$$dU = -P dV + T dS, \quad (9.4)$$

- **ENTHALPY**

Define a new characteristic function H , called *enthalpy*, using Eq. (9.2) to obtain

$$H \equiv U + PV. \quad (9.5)$$

Since U , P , and V are all state functions, H is also a state function. In differential form,

$$dH = dU + PdV + VdP$$

But from eq.(9.4), then

$$dH = -PdV + Tds + PdV + VdP$$

$$dH = T ds + V dP \dots \dots (9.6)$$

where H is a function characterized by P and S .

- **HELMHOLTZ FREE ENERGY**

Equation (10.4) may be rewritten as

$$dU = T dS - P dV,$$

in order to generate a characteristic function other than enthalpy, namely, the *Helmholtz function* A , given by the Legendre transform

$A \equiv U - TS,$	(9.7)
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which is also a state function. In differential form,

$dA = -S dT - P dV,$	(9.8)
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where A is a function of T and V .

The last characteristic function, known as the *Gibbs function* G , is generated by a Legendre transformation of

$$dH = T dS + V dP,$$

Then

$G \equiv H - TS,$	(9.9)
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which is also a state function. In differential form,

$dG = V dP - S dT,$	(9.10)
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where G is a function characterized by P and T .

In terms of the state functions so far defined, we have written four differential equations that are formulations of the first law, namely,

$$dU = -P dV + T dS,$$

$$dH = V dP + T dS,$$

$$dA = -P dV - S dT,$$

and

$$dG = V dP - S dT.$$

The characteristic functions $U(V, S)$, $H(P, S)$, $A(V, T)$, and $G(P, T)$ are known as thermodynamic potential functions.

Now

$$U(V, S)$$

Then we can write

$$dU = \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial S}\right)_V dS,$$

from comparison with Eq. (10.4), that

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \quad \text{and} \quad \left(\frac{\partial U}{\partial S}\right)_V = T. \quad (9.11)$$

9.5 : MAXWELL RELATIONS

We have seen that the hydrostatic properties of a pure substance are conveniently represented in terms of the differentials of any of these four functions:

$$dU = -P dV + T dS,$$

$$dH = V dP + T dS,$$

$$dA = -P dV - S dT,$$

$$dG = V dP - S dT.$$

From (10.11), then

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

But

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

Then

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

Then

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \text{First Maxwell Equation}$$

Similarly from eq.(10.6);

$$dH = Tds + VdP \dots (9.12)$$

And $H = H(S, P)$ as exact differential is written as

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP \dots (9.13)$$

Comparing eqs.(10.6 , 10.7), then

$$T = \left(\frac{\partial H}{\partial S}\right)_P \quad \text{and} \quad V = \left(\frac{\partial H}{\partial P}\right)_S$$

$$\left(\frac{\partial}{\partial V}\right)_S \left(\frac{\partial H}{\partial S}\right)_P = \left(\frac{\partial}{\partial S}\right)_V \left(\frac{\partial H}{\partial V}\right)_S$$

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

Then

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P, \text{ Second maxwell equation}$$

Similarly dA is ;

$$dA = -PdV - SdT \dots (9.14)$$

And $A = A(V, T)$ as exact differential is written as

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT \dots (9.15)$$

Comparing eqs.(10.8 , 10.9) ,then

$$-P = \left(\frac{\partial A}{\partial V}\right)_T \quad \text{and} \quad -S = \left(\frac{\partial A}{\partial T}\right)_V$$

$$\left(\frac{\partial}{\partial V}\right)_T \left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial A}{\partial V}\right)_T$$

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

Then

$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V, \text{Third maxwell equation}$
--

Similarly dG is;

$$dG = VdP - SdT \dots (9.16)$$

And $G = G(P, T)$ as exact differential is written as

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT \dots (9.17)$$

Comparing eqs.(10.10 , 10.11) ,then

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

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

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

Then

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T, \text{ Fourth maxwell equation}$$

Then in conclusion we can write the following

1. $dU = T dS - P dV$; hence, $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$.
2. $dH = T dS + V dP$; hence, $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$.
3. $dA = -S dT - P dV$; hence, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$.
4. $dG = -S dT + V dP$; hence, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$.

Problem (10.1)

Given the relations

1. $dU = T dS - P dV$
2. $dH = T dS + V dP$;
3. $dA = -S dT - P dV$;
4. $dG = -S dT + V dP$;

Derive the following Maxwell's equations

$$1. \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$2. \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$3. \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$4. \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

(Look the answer above)