

Study Unit 2: Limitations and Application of First Law, Second Law and Thermodynamics Potential

Introduction

This study unit is a continuation of the study unit 1, it discusses in further the limitations and application of the first law of thermodynamics. The unit presented the Second law (Kalvin Planks and Clausius Statements), Carnot cycles and the stages involved are also discussed in details and the unit concludes with thermodynamics potentials and their derivations.

Learning Outcomes of Study Unit 2:

At the end of this unit, you should be able to;

- i Discuss limitations of the first law of thermodynamics as it relates to thermal reservoir, heat engine and heat pump
- ii Explain the application of first law and derive the mathematical implications of each
- iii Define and explain the principles of Second Law of thermodynamics
- iv Describe Carnot Cycle and explain the stages involved in the process
- v Define entropy and apply it to Second Law
- vi Derive the mathematical expression for thermodynamics potentials.

Limitations of First Law:

The first law of thermodynamics is a law of conservation of energy. It does not specify the direction of the process. All spontaneous processes processed in one direction only. The first law of thermodynamics does not deny the feasibility of a process reversing itself. The first law of thermodynamics does not provide answers to the following questions.

Is a particular process / reaction feasible?

To what extent do the process / reaction proceed?

Is complete conversion of internal energy into work possible?

There exists a law which determines the direction in which a spontaneous process proceeds. The law, known as the second law of thermodynamics, is a principle of wide generality and provides answer to the above questions.

Thermal reservoir

It is a large body from which a finite quantity of energy can be extracted or to which a finite quantity of energy can be added as heat without changing its temperature. A source is a thermal reservoir at high temperature from which a heat engine receives the energy as heat. A sink is a low temperature thermal reservoir to which a heat engine rejects energy as heat.

Heat Engine

A heat engine is a device which converts the energy it receives as heat, into work. A heat engine is a system that converts heat or thermal energy, and chemical energy to mechanical energy, which can then be used to do mechanical work. It does this by bringing a working substance from a higher state temperature to a lower state temperature

It is a cyclically operating device. It receives energy as heat from a high temperature body, converts part of it into work and rejects the rest to a low temperature body. A thermal power plant is an example of a heat engine.

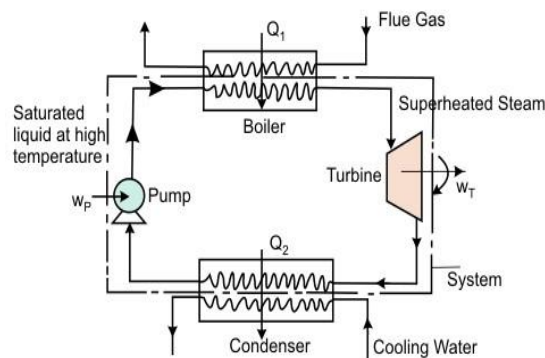


Figure 2.1: Heat Engine

In the boiler, the working fluid receives a certain amount of heat (Q_1) from the hot combustion products. The superheated steam enters a turbine where it undergoes expansion performing the shaft work (W_T). The low pressure steam enters a condenser where it exchanges energy as heat at constant pressure with the cooling water and emerges as the condensate. The condensate rejects a certain amount of heat (Q_2) to the cooling water. The low pressure condensate from the condenser enters the pump. Work (W_P) is done on the pump to elevate the condensate to the boiler pressure and return it to the boiler.

$$\text{Work done by the system} = W_T - W_P$$

$$\text{Energy absorbed as heat by the system} = Q_1$$

$$\text{Energy rejected as heat by the system} = Q_2$$

According to first law of thermodynamics, the heat and work interaction are related by the equation.

$$\oint dQ = \oint dW$$

Finally, the thermal efficiency (η) of a heat engine can be expressed as

$$\begin{aligned}
 \eta &= \frac{(\text{Energy absorbed as heat} - \text{Energy rejected as heat})}{\text{Energy absorbed as heat}} \\
 &= \frac{\text{Net work done}}{\text{Energy absorbed as heat}} = \frac{W_T - W_P}{Q_1}
 \end{aligned}$$

or,

$$\eta = \frac{Q_1 - Q_2}{Q_1}$$

Heat pump

Heat Pump is cyclically operating device which absorbs energy from a low temperature reservoir and reject energy as heat to a high temperature reservoir when work is performed on the device. Its objective is to reject energy as heat to a high temperature body (space heating in winter). The atmosphere acts as the low temperature reservoir.

Refrigerator

A refrigerator is a cyclically operating device which absorbs energy as heat from a low temperature body and rejects energy as heat to a high temperature body when work is performed on the device. The objective of this device is to refrigerate a body at low temperature. Usually it uses atmosphere as the high temperature reservoir.

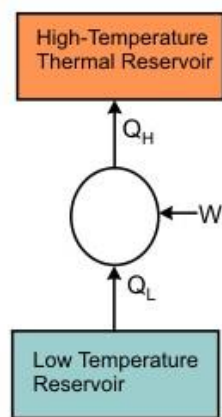


Figure 2.2: Heat pump/Refrigerator

Parameters/Coefficient of performance

Let Q_H and Q_L represents the amount of energy absorbed as heat from the low temperature reservoir and the energy rejected as heat to the high temperature reservoir respectively, Let W be the work done on the device to accomplish the task.

Q_H and $Q_L = W$

Therefore,

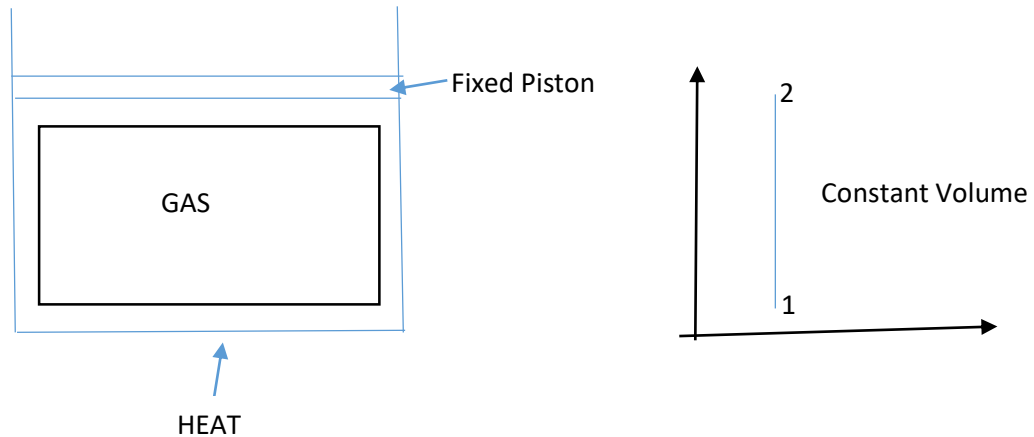
$$(COP)_R = \frac{Q_L}{W} = \frac{Q_L}{(Q_H - Q_L)}$$

and

$$(COP)_{HP} = \frac{Q_H}{W} = \frac{Q_H}{(Q_H - Q_L)}$$

Application of First Law of Thermodynamics to Non-Flow or Close System

1. Reversible Constant Volume (Isochoric Process)- No work is done on or by the system-
The volume is constant



From

$$Q = (U_2 - U_1) + W$$

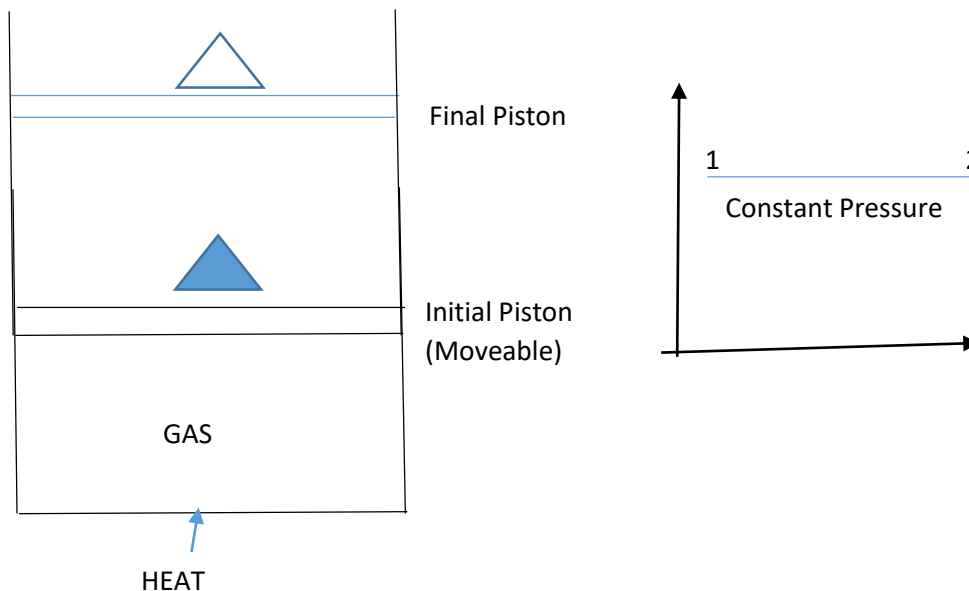
$$\text{Work done, } W = \int_1^2 P dv = 0$$

$$Q = (U_2 - U_1) = C_v (T_2 - T_1)$$

$$Q = MC_v (T_2 - T_1)$$

mass = m

2. Reversible Constant Pressure (Isobaric Process)



The following occur in the isobaric process; Boundary of the system if flexible, pressure rises when heat is supplied, boundary move against an external resistance. Since the piston is

pushed through a certain distance by the force exerted by the gas, then the work done is done by the gas on its surrounding.

From

$$Q = (U_2 - U_1) + W$$

$$\text{Work done, } W = \int_1^2 P dv = P(V_2 - V_1)$$

$$Q = (U_2 - U_1) + P(V_2 - V_1)$$

$$Q = U_2 - U_1 + PV_2 - PV_1$$

$$Q = (U_2 + PV_2) - (U_1 + PV_1)$$

$$\text{From } h = U + PV$$

$$\text{Then } Q = h_2 - h_1$$

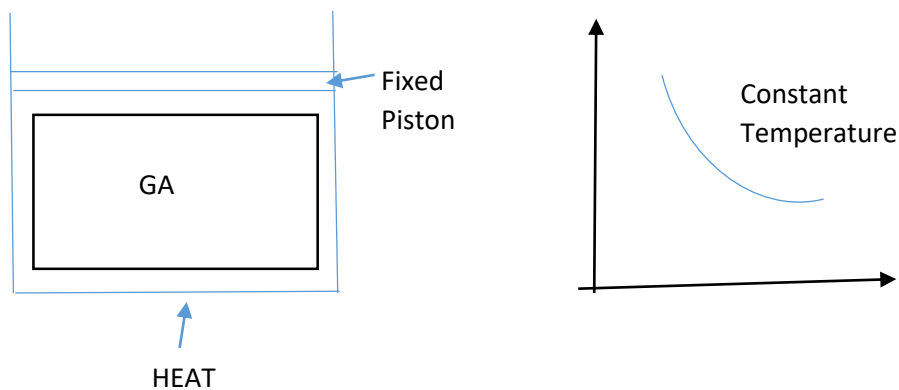
$$Q = C_p (T_2 - T_1)$$

Where h is enthalpy, C_p is specific heat capacity for mass m of a working system

$$\text{Then } Q = H_2 - H_1$$

$$Q = mC_p (T_2 - T_1)$$

3. Reversible Temperature (Isothermal Process)



From

$$Q = (U_2 - U_1) + W$$

$$Q = C_v (T_2 - T_1) + w$$

$$Q = 0 + w$$

$$\text{Work-done, } W = \int_1^2 P dv$$

$$PV = C \text{ (constant)}$$

$$\text{Therefore } P = \frac{C}{V}$$

$$\text{From } W = \int_{V_2}^{V_1} C \frac{dv}{v} = \ln V_{V_1}^{V_2} = C \log_e \frac{V_2}{V_1}$$

$$W = C \ln(V_2 - V_1)$$

$$\text{From } C = P_1 V_1 = P_2 V_2$$

$$W = P_1 V_1 \log_e \frac{V_2}{V_1} \text{ or } P_2 V_2 \log_e \frac{V_2}{V_1}$$

$$\text{Therefore } Q = P_1 V_1 \log_e \frac{V_2}{V_1}$$

4. Reversible Adiabatic Process- An adiabatic process is one in which no heat is transferred to or from the fluid during the process. In an adiabatic process PV^γ is constant

In an adiabatic expansion, the work-done W by the fluid is at the expense of the reduction in the internal energy of the fluid.

In an adiabatic compression process all the work-done on the fluid goes to increase the internal energy of the fluid.

5. Polytropic Process – A process which is described well by an equation of the form $PV^n = \text{Constant } (C)$, where n is known as the polytropic exponent

Activity

1. From $dQ = dU + dW$, show that PV^γ is constant for an adiabatic process.

2. Hence or otherwise show that the expression for work-done in an adiabatic process for a perfect gas is $W = R \frac{(T_2 - T_1)}{\gamma - 1}$

3. From the expressions in the isothermal, isochoric, isobaric and adiabatic processes discussed above, use the information to compute the work-done under a polytropic process, $W = \frac{P_2 V_2 - P_1 V_1}{1 - n}$ if $n \neq 1$

Second Law of Thermodynamics

KELVIN PLANCK STATEMENT: It is impossible to construct a cyclically operating device such that it produces no other effect than the absorption of energy as heat from a single thermal reservoir and performs an equivalent amount of work.

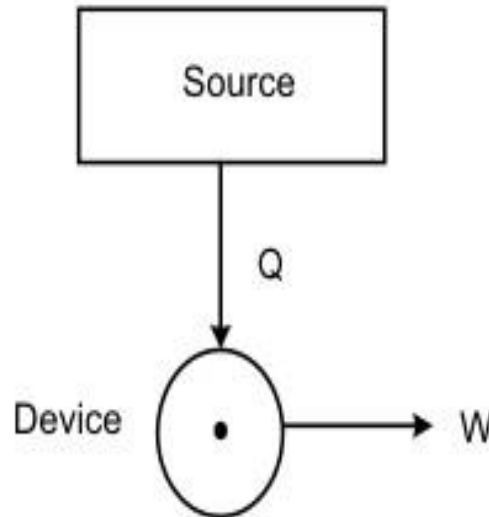


Figure 2.3: Kelvin Planck Statement

CLAUSIUS STATEMENT: Heat always flows from a body at higher temperature to a body at a lower temperature. The reverse process never occurs spontaneously. Clausius statement of the second law gives: It is impossible to construct a device which, operating in a cycle, will produce no effect other than the transfer of heat from a low-temperature body to a high temperature body.

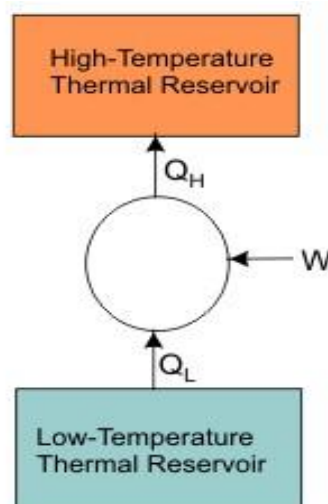


Figure 2.4: Clausius Statement

Equivalence / Corollaries

Let us suppose that the Kelvin Planck statement is incorrect.

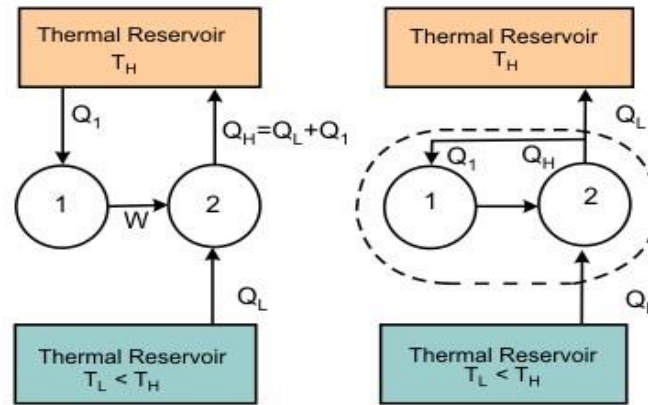


Figure 2.5: Equivalence of Kelvin Planck and Clausius Statement

It is possible to construct a device I which, working cyclically, absorbs energy as heat from a source at temperature T_H and performs an equivalent amount of work. Next consider a device II which absorbs amount of energy from a low temperature body at T_L and delivers energy as heat to a high temperature reservoir at T_H . To accomplish this, work is done on the device. The device II does not violate the Clausius statement. For device II, we can write. Now combine I and II. The work delivered by device I is used by device, II. This combined device (which is no more aided by any external agency) working cyclically, is not producing any effect other than the transfer of energy as heat from the low temperature reservoir to the high temperature reservoir. This is in violation of the Clausius statement.

To prove that violation of the Clausius statement leads to violation of Kelvin Planck statement, let us assume that the Clausius statement is incorrect. That is, it is possible to construct a device I such that it transfers energy as heat from a body at lower temperature to a body at higher temperature unaided by any external agency. Consider another device II which receives energy as heat from a body at higher temperature, delivers work and rejects energy as heat to the body at a low temperature. Device II does not violate Kelvin Planck statement.

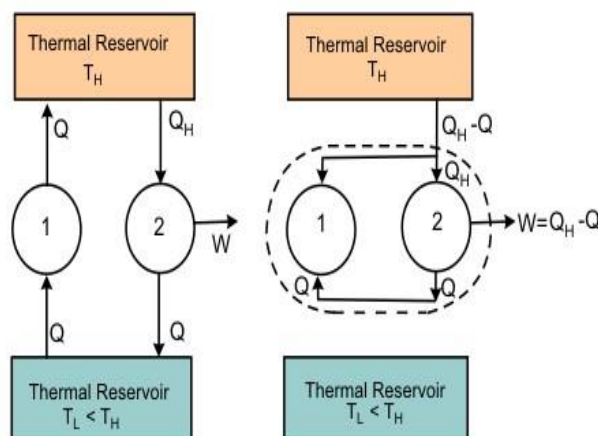


Figure 2.6: Equivalence of Clausius Kelvin and Planck Statement

PMM of Second kind

A perpetual motion machine of the second kind, or PMM2 is one which converts all the heat input into work while working in a cycle.

Carnot's principle:

The most efficient heat engine cycle is the Carnot cycle, consisting of two isothermal processes and two adiabatic processes. The Carnot cycle can be thought of as the most efficient heat engine cycle allowed by physical laws. When the second law of thermodynamics states that not all the supplied heat in a heat engine can be used to do work, the Carnot efficiency sets the limiting value on the fraction of the heat which can be so used.

In order to approach the Carnot efficiency, the processes involved in the heat engine cycle must be reversible and involve no change in entropy. This means that the Carnot cycle is an idealization, since no real engine processes are reversible and all real physical processes involve some increase in entropy.

Carnot cycle and its specialties

The Carnot cycle when acting as a heat engine consists of the following steps:

1. Reversible isothermal expansion of the gas at the "hot" temperature, T_1 (isothermal heat addition or absorption). During this step the gas is allowed to expand and it does work on the surroundings. The temperature of the gas does not change during the process, and thus the expansion is isothermal. The gas expansion is propelled by absorption of heat energy Q_1 and of entropy $\Delta S = Q_1/T_1$ from the high temperature reservoir.
2. Isentropic (reversible adiabatic) expansion of the gas (isentropic work output). For this step the mechanisms of the engine are assumed to be thermally insulated, thus they neither gain nor lose heat. The gas continues to expand, doing work on the surroundings, and losing an equivalent amount of internal energy. The gas expansion causes it to cool to the "cold" temperature, T_2 . The entropy remains unchanged.
3. Reversible isothermal compression of the gas at the "cold" temperature, T_2 . (isothermal heat rejection). Now the surroundings do work on the gas, causing an amount of heat energy Q_2 and of entropy $\Delta S = Q_2/T_2$ to flow out of the gas to the low temperature reservoir. (This is the same amount of entropy absorbed in step 1, as can be seen from the Clausius inequality.)
4. Isentropic compression of the gas (isentropic work input). Once again the mechanisms of the engine are assumed to be thermally insulated. During this step, the surroundings do work on the gas, increasing its internal energy and compressing it, causing the temperature to rise to T_1 . The entropy remains unchanged. At this point the gas is in the same state as at the start of step 1.

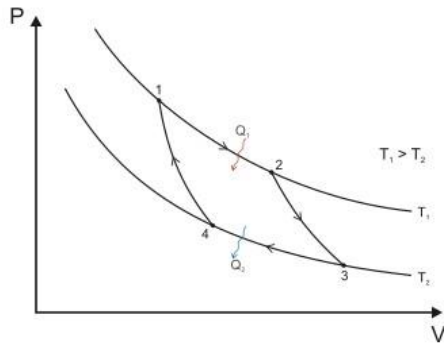


Figure 2.7: Carnot Cycle PV diagram

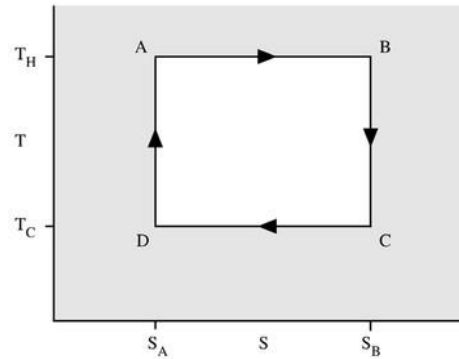


Figure 2.8: Carnot Cycle TS diagram

Thermodynamic scale of Temperature

A temperature scale, which does not depend on the thermodynamic property of the substance can be established by making use of the fact that the efficiency of a reversible heat engine does not depend on the nature of the working fluid but depends only upon the temperature of the reservoirs between which it operates. The establishment of thermodynamic temperature scale is also a consequence of the second law of thermodynamics. It can be understood by the following figure.

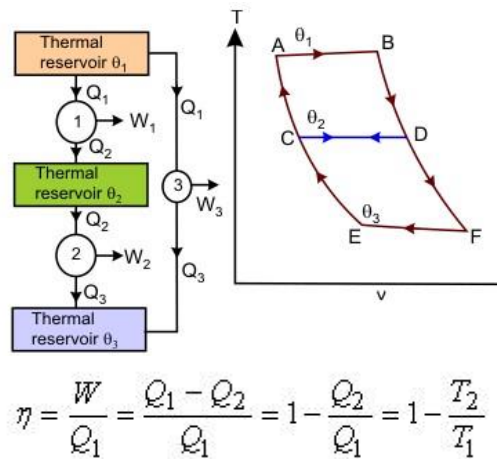


Figure 2.9: Thermodynamic scale of Temperature

Clausius Inequality

Consider a system undergoing a reversible cycle. The given cycle may be sub-divided by drawing a family of reversible adiabatic lines. Every two adjacent adiabatic lines may be joined by two reversible isotherms.

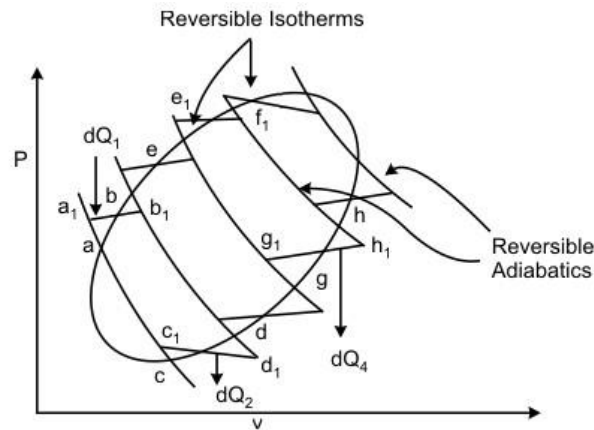


Figure 2.10: Clausius Inequality

If similar equations are written for all the elementary cycles, then

$$\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} + \frac{dQ_3}{T_3} + \frac{dQ_4}{T_4} = 0$$

or,

$$\oint_R \frac{dQ}{T} = 0$$

Similarly, for the irreversible cycle $e_1 g_1 h_1 f_1$

$$\frac{dQ_3}{T_3} + \frac{dQ_4}{T_4} < 0$$

Summing up all elementary cycles

$$\oint_{IR} \frac{dQ}{T} < 0$$

The above two conclusions about reversible and irreversible cycles can be generalized as

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

The equality holds good for a reversible cycle and the inequality holds good for an irreversible cycles. The complete expression is known as Clausius Inequality.

Entropy

Entropy is a measure of the "disorder" of a system. The disorder refers to is really the number of different microscopic states a system can be in, given that the system has a particular fixed composition, volume, energy, pressure, and temperature. Clausius inequality can be used to analyze the cyclic process in a quantitative manner. The second

law became a law of wider applicability when Clausius introduced the property called entropy. By evaluating the entropy change, one can explain as to why spontaneous processes occur only in one direction.

$$\int \frac{dQ}{T}$$

$(dQ/T)_R$ is

Consider that, it is possible to connect the states 1 and 2 by several reversible paths and see that has the same value irrespective of the path as long as the paths are reversible. Therefore, an exact differential of some function which we identify as entropy. Hence it can be said that there exists a function S , called entropy, the change in entropy is expressed as

$$S_2 - S_1 = \Delta S = \int_1^2 dS = \int_1^2 (dQ/T)_R$$

The following facts should be kept in mind while calculating the change in entropy for a process

1. $ds = (dQ/T)_R$ For a reversible process
2. Entropy is a state function.
3. The entropy change of a system is determined by its initial and final states only, irrespective of how the system has changed its state. In analyzing irreversible processes, it is not necessary to make a direct analysis of the actual process. One can substitute the actual process by a reversible process connecting the final state to the initial state, and the entropy change for the imaginary reversible process can be evaluated.

Principle of Entropy Increase

Now let us apply the above results to evaluate the entropy of the universe when a system interacts with the surroundings.

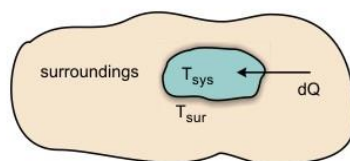


Figure 2.11: Principle of Entropy Increase

Temperature of the system = T_{sys}

and,

$$T_{sur} > T_{sys}$$

If the energy exchange takes place, dQ will be the energy transfer from the surroundings to the system.

$$dS_{sys} = dQ / T_{sys}$$

$$dS_{sur} = dQ / T_{sur}$$

$$dS_{uni} = dS_{sys} + dS_{sur}$$

$$dS_{uni} = \frac{dQ}{T_{sys}} - \frac{dQ}{T_{sur}} > 0 \quad [\text{since } T_{sur} > T_{sys}]$$

So,

Now let us redefine a system which includes our earlier system and its surroundings. Then

$$(\Delta S)_{sys} > 0, \text{ for an isolated system}$$

Through generalization we can write for an isolated system

$$(\Delta S)_{sys} \geq 0$$

Examine the statement critically. For a reversible process it is equal to zero. For an irreversible process it is greater than zero.

Similarly it is possible to write $(\Delta S)_{uni} \geq 0$. The equality sign holds good if the process undergone is reversible; the inequality sign holds good if the process undergone is irreversible.

Finally entropy increase means

- The energy of the universe is constant (first law).
- The entropy of the universe tends towards a maximum (second law)

Energy Equation, Availability and Irreversibility

Available Energy: In order to determine that part of the energy which can be converted into work by an engine, we require consider a thermal reservoir at constant temperature T from which a quantity of energy Q is being absorbed as heat.

Consider the Carnot cycle as shown in a T - S diagram below:

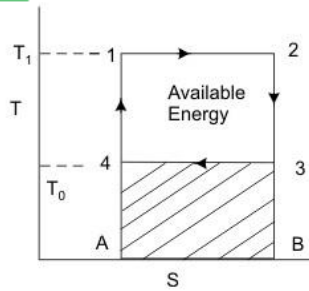


Figure 2.12: Carnot TS Diagram

The area 1234 represents the portion of energy delivered as work by the reversible engine and is called available energy. The area 43BA represents the portion of the energy which is rejected to the atmosphere. The portion of energy is not available for conversion into work is called unavailable energy. Therefore, the available energy represents the portion of the energy supplied as heat which can be converted into work by means of a reversible engine. It is also known as EXERGY.

$$\text{Then the initial available energy} = Q \left(1 - \frac{T_0}{T_1} \right)$$

$$\text{the final available energy} = Q \left(1 - \frac{T_0}{T_2} \right)$$

Therefore the loss of available energy

$$\begin{aligned}
 &= Q \left[\left(1 - \frac{T_0}{T_1} \right) - \left(1 - \frac{T_0}{T_2} \right) \right] = T_0 \left[\frac{Q}{T_2} - \frac{Q}{T_1} \right] \\
 &= T_0 \Delta S_{\text{un}}
 \end{aligned}$$

The availability of a given system is defined as the maximum useful work that can be obtained in a process in which the system comes to equilibrium with the surroundings or attains a dead state. Clearly, the availability of a system depends on the condition of the system as well as those of the surroundings.

Thermodynamic Potentials

Eight properties of a system, namely pressure (p), volume (v), temperature (T), internal energy (u), enthalpy (h), entropy (s), Helmholtz function (f) and Gibbs function (g). h, f and g are sometimes referred to as thermodynamic potentials.

$g = h - T.s$ is known as Gibb's function or free energy function $f = u - T.s$ is known as Helmholtz function. This gives maximum possible output when the heat Q is transferred at constant temperature and is the case with a very large source.

Gibbs and Helmholtz Functions

The work done in a non-flow reversible system (per unit mass) is given by :

$$\begin{aligned}
 W &= Q - (U_0 - U_1) \\
 &= T.ds - (U_0 - U_1)
 \end{aligned}$$

$$T(S_0 - S_1) - (U_0 - U_1)$$

$$\text{i.e., } W = (U_1 - TS_1) - (U_0 - TS_0)$$

The term $(u - Ts)$ is known as Helmholtz function. This gives maximum possible output when the heat Q is transferred at constant temperature and is the case with a very large source. If work against atmosphere is equal to $p_0(V_0 - V_1)$, then the maximum work available,

$$\begin{aligned} W &= W - \text{work against atmosphere} \\ &= W - P_0(V_0 - V_1) \\ &= (U_1 - TS_1) - (U_0 - TS_0) - P_0(V_0 - V_1) \\ &= (U_1 + P_0 V_1 - TS_1) - (U_0 + P_0 V_0 - TS_0) \\ &= (h_1 - TS_1) - (h_0 - TS_0) \end{aligned}$$

i.e., $W_{\max} = g_1 - g_0$ where $g = h - Ts$ is known as Gibb's function or free energy function.

The maximum possible available work when system changes from 1 to 2 is given by

$$W_{\max} = (g_1 - g_0) - (g_2 - g_0) = g_1 - g_2$$

Maxwell Relations

If dx is called an exact differential, then

$$dx = Mdy + Ndz$$

Where

$$M = \left(\frac{\partial x}{\partial y}\right)_z \text{ and } N = \left(\frac{\partial x}{\partial z}\right)_y$$

We know from the first law of thermodynamics,

$$\begin{aligned} dQ &= du + pdv \\ Tds &= du + pdv \\ du &= Tds - pdv \text{----- eq. 1} \end{aligned}$$

We know enthalpy as $h = u + pv$

$$\begin{aligned} dh &= du + pdv + vdp \\ dh &= Tds + vdp \text{----- eq. 2} \end{aligned}$$

Helmholtz free energy function

$$\begin{aligned} f &= u + TS \\ df &= du - Tds - sdT \\ df &= -pdv - sdt \text{-----eq. 3} \end{aligned}$$

Gibb's free energy function

$$\begin{aligned} g &= h - Ts \\ dg &= dh - Tds - sdT \\ dg &= vdp - sdT \text{-----eq. 4} \end{aligned}$$

Therefore, the Maxwell's equations can be rewritten as follows when above equations are considered as exact differentials.

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T$$

Elementary Treatment of the Third Law of Thermodynamics

'Third law of thermodynamics', an independent principle uncovered by 'Nernst' and formulated by 'Planck', states that the "Entropy of a pure substance approaches zero at absolute zero temperature." This fact can also be corroborated by the definition of entropy which says it is a measure of molecular disorderliness. At absolute zero temperature substance molecules get frozen and do not have any activity, therefore it may be assigned zero entropy value at crystalline state. Although the attainment of absolute zero temperature is impossible practically, however theoretically it can be used for defining absolute entropy value with respect to zero entropy at absolute zero temperature. Second law of thermodynamics also shows that absolute zero temperature can't be achieved. Third law of thermodynamics is of high theoretical significance for the sake of absolute property definitions and has found great utility in thermodynamics.

Practicing Questions

1. A reversible heat engine operates between two reservoirs at temperature 700°C and 50°C. The engine drives a reversible refrigerator which operates between reservoirs at temperatures of 50°C and -25°C. The heat transfer to the engine is 2500KJ and the net-work output of the combined engine refrigerator plant is 400KJ.
 - i. Determine the heat transfer to the refrigerator and the net heat transfer to the reservoir at 50°C.
 - ii. Reconsider (i) given that the efficiency of the heat engine and the COP of the refrigerator are each 45per cent of their maximum possible values.
2. Define the following thermodynamic potentials;
 - i. Entropy
 - ii. Helmholtz function
 - iii. Gibbs function
3. From equation of first law of thermodynamics, $dQ = du + Pdv$ derive expression for each thermodynamic potential in question 2.
4. An iron cube at a temperature of 400°C is dropped into an insulated bath containing 10kg water at 25°C. The water finally reaches a temperature of 50°C at steady state. Given that the specific heat of water is equal to 4186J/KgK. Find the entropy changes for the iron cube and the water. Is the process resersible? If so why?

Reference

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