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Objectives

By reading this chapter, you will be able to understand;

- ✓ How thermodynamic variables can be combined to have state functions with units of energy.
- ✓ The definitions of thermodynamic potentials.
- ✓ The significance and applications of thermodynamic potentials.
- ✓ How Maxwell's equationscan be obtained using thermodynamic potentials.

11.1 Introduction

We know that the internal energy (U) of a thermodynamic system is a state function which means that a system undergoes the same change in U when moved from one equilibrium state to another, irrespective of the path followed. This path independence of internal energy makes it very useful, however, not a uniquely useful quantity. There could be some other combinations of the state variables (i.e. pressure p, volume V, temperature T, and entropy S) which when added with the internal energy function may result quantities having dimensions of energy and preserve the nature of path independence. These new state functions are very useful and termed as **thermodynamic potentials**e.g. the functions like U + TS, U - pV, U + 2pV - TS, and U - tpV + 3TS etc. However, all such combinations may not be helpful in the study of a thermodynamic system but the combinations like U + pV, U - TS, and U + pV - TS are found to have significant role and are named as enthalpy (H), Helmholtz function (F), and Gibbs function (G) respectively. All the thermodynamic properties of a system can be calculated by differentiating these functions. In this lesson, we explored the importance and usefulness of these potentials. However, at first, let us remind about the internal energy function.

11.2 Internal energy

The internal energy can be defined as the total energy (kinetic and potential) contained in a thermodynamic system. Mathematically, the change in the internal energy dU is may be expressed as;

$$dU = \Delta Q - \Delta W \tag{11.1}$$

and with the definition of entropy change $(dS = \frac{dQ}{T})$ and work (dW = pdV), dU can be written as

$$dU = TdS - pdV (11.2)$$

In the above equation, we expressed dU in terms of **natural variables** S and/or V. As discussed in the introduction, we can calculate other thermodynamic properties of the system using internal energy:

From equation (11.2), we can calculate the temperature and pressure by differentiating U;

$$\left(\frac{\partial U}{\partial S}\right)_{V} = T, and \left(\frac{\partial U}{\partial V}\right)_{S} = -p$$
 (11.3)

Now, for reversible isochoric processes, the change in internal energy is given by;

$$dU = TdS$$
 $(as dV = 0)$

And heat transferred to the system;

$$dU = dQ \ (reversible) = C_V \ dT \quad \left(as \ dS = \frac{dQ}{T}, for \ reversible \ processes \right)$$
 (11.4)

Hence the net change in the internal energy (or heat transferred) can be calculated as;

$$\Delta U = U_2 - U_1 = \int dU = \int_{T_*}^{T_2} C_V dT$$
 (11.5)

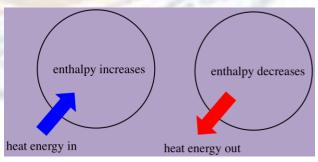
It is clear from above discussion that in order to calculate the internal energy change (or reversible heat) in an isochoric process, we have to make a constraint on volume which is not easier to apply experimentally. However, a laboratory experiment open to air is usually at constant pressure (atmospheric pressure) and this constraint is relatively easier to apply on the systems. So, the value of reversible heat transferred can easily obtained by imposing isobaric constraints rather than that of isochoric and for that we have another important thermodynamic potential described next.

11.3 Enthalpy (H)

It is a total heat function defined by:

$$H = U + pV \tag{11.6}$$

It could also be understood as the total heat transferred (evolved/absorbed) to the system at constant pressure. If we add heat to the system at constant pressure, the enthalpy of the system increases and it decreases when heat is provided by the system to its surroundings.



For an infinitesimal reversible process, the change in the enthalpy can be expressed as;

$$dH = dU + pdV + VdP$$

$$or, dH = TdS - pdV + pdV + VdP$$

$$or, dH = TdS + VdP (11.7)$$

Hence, for isobaric reversible process;

$$dH = TdS = dQ (reversible) = C_p dT (as dp = 0)$$

And, the net change in enthalpy can be obtained as;

$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_2} C_p \, dT \tag{11.8}$$

From equation (11.7), it is also clear that for isentropic and isobaric processes, the enthalpy remains constant i.e.

$$dH = TdS + VdP = 0$$
, (as dS and dp will be zero)

$$or$$
 $H = constant$

The parameters temperature and volume can be expressed in terms of enthalpy as:

$$\left(\frac{\partial H}{\partial S}\right)_p = T$$
, and $\left(\frac{\partial H}{\partial p}\right)_V = V$ (11.9)

Now, as can be seen from the discussion about U and H that both these potential functions involve entropy as one of their natural variables which is not an easy parameter to control in the laboratory. Temperature and pressure, on the other hand, can easily be controlled and vary in the laboratory. The next two potentials are having these parameters as their natural variables.

11.4 Helmholtz Function (F)

H. V. Helmholtz (1821-1894), a German physician and physicist, contributed significantly to multiple fields of modern science. Various important concepts/theories such as mathematics of the eye, theories of vision, visual perception of space, color vision research, sensation of tone, perception of sound, and empiricism have been proposed by him in the field of physiology and psychology. He significantly made contribution to the physics in the form of his theories on the of energy; work in electrodynamics, conservation thermodynamics, and mechanical foundation on thermodynamics. The largest German association of research institutions was given name "the Helmholtz Association" after him.



H. V. Helmholtz (Image taken from Wikipedia)

The Helmholtz function (F), also known as Helmholtz free energy is defined as:

$$F = U - TS \tag{11.10}$$

The small change in Helmholtz function (dF) can be expressed as:

$$dF = dU - TdS - SdT$$

$$= TdS - pdV - TdS - SdT$$

$$dF = -pdV - SdT$$
(11.11)

It can easily be seen that the Helmholtz function remains constant during an isochoric and isothermal process *i.e.* dF = 0, or F = constant.

Equation (11.10) reflects that V and T are the natural variables of F i.e. F = F(V,T). Also, pressure and entropy can be expressed in terms of F as:

$$\left(\frac{\partial F}{\partial V}\right)_T = -p, and \left(\frac{\partial F}{\partial T}\right)_V = -S$$
 (11.12)

For the isothermal processes dT = 0, and hence equation (11.12) yields;

$$dF = -pdV$$

And hence the net change in F of a system during an isothermal process can be calculated as;

$$\Delta F = F_2 - F_1 = -\int_{V_1}^{V_2} p dV \tag{11.13}$$

From above equation, it is clear that a positive change in the Helmholtz function represents the work done on the system by its surroundings and decrease the decrease in its value indicates the work is performed by the system on its surroundings. So, F gives the value of maximum amount of workthat can be obtained out of a system at constant temperature. The system can work on its surroundings until F reaches to a minimum.

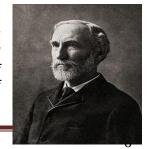
11.5 Gibbs free energy (G)

The Gibbs free energy G (or Gibbs function), also known as free enthalpy is defined as a thermodynamic potential that measures the "useful" work obtainable from a thermodynamic system at a constant temperature and pressure. Mathematically, it may be expressed as;

$$G = H - TS \tag{11.14}$$

The small change in Gibbs function could be obtained as;

Josiah Willard Gibbs(1839–1903) was an American scientist who made important theoretical contributions to physics, chemistry, and mathematics. His applied work on thermodynamics was transformed physical chemistry into a rigorous deductive science. He contributed significantly to statistical mechanics and explained the laws of thermodynamics as the consequences of the statistical properties of large ensembles of particles. In mathematics, he invented modern



J. W. Gibbs (Image from Wikipedia)

vector calculus independently. Gibbs also worked on the application of Maxwell's equations to problems in physical optics.

$$dG = dH - TdS - SdT$$

$$= d(U + pV) - TdS - SdT$$

$$= dU + pdV + Vdp - TdS - SdT$$

$$= TdS - pdV + pdV + Vdp - TdS - SdT$$

$$dG = -SdT + Vdp$$
(11.15)

Clearly, for isobaric and isothermal processes, dG = 0, i.e.G = constant. The natural variables of G are T and p [see equation 11.15)] and are rather convenient to control and vary in the laboratory.

The expressions for entropy and volume in terms of G can be written as;

$$\left(\frac{\partial G}{\partial T}\right)_p = -S, and \left(\frac{\partial G}{\partial p}\right)_V = -V$$
 (11.16)

Example 1: Establish the following thermodynamic relations.

(a)
$$C_V = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V$$
 and (b) $C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_p$

Proof: (a) From equation (11.12), we have; $\left(\frac{\partial F}{\partial T}\right)_V = -S$

Partial differentiation of above equation gives;

$$\frac{\partial}{\partial T} \left(\frac{\partial F}{\partial T} \right)_{V} = -\left(\frac{\partial S}{\partial T} \right)_{V}$$

$$or \qquad T \left(\frac{\partial^{2} F}{\partial T^{2}} \right)_{V} = -\left(\frac{\partial TS}{\partial T} \right)_{V}$$

$$or \qquad T \left(\frac{\partial^{2} F}{\partial T^{2}} \right)_{V} = -\left(\frac{\partial Q}{\partial T} \right)_{V} = -C_{V}$$

$$or \qquad T \left(\frac{\partial^{2} F}{\partial T^{2}} \right)_{V} = -C_{V}$$

(b)Using equation(11.16) i.e. $\left(\frac{\partial G}{\partial T}\right)_p = -S$, and following in the same way as above gives the result.

Example 2: Prove the following Gibbs-Helmholtz relations:

(a)
$$U = F - T \left(\frac{\partial F}{\partial T} \right)_V$$
 and (b) $H = G - T \left(\frac{\partial G}{\partial T} \right)_p$

Proof: From the definition of Helmholtz function *i.e.* F = U - TS and with the expression given in equation (11.12) i.e.

$$\left(\frac{\partial F}{\partial T}\right)_{V} = -S$$

or
$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

Putting this value of S in F = U - TS, we have;

$$F = U - T \left[- \left(\frac{\partial F}{\partial T} \right)_{V} \right]$$

$$or \quad U = F - T \left(\frac{\partial F}{\partial T} \right)_V$$

(b)With the definition of Gibbs function [equation (11.14) and the equation (11.16), we can have the required result by following in the same way as above.

11.6 Maxwell's relations

Maxwell's relations are of great importance as they provide relationships between measurable thermodynamic quantities and those which either can not be measured or are difficult to measure. In particular, the parameters like temperature, pressure and volume of a thermodynamic system can be measured experimental techniques where as it are difficult to measure entropy experimentally. We will see that by using Maxwell's relations one can determine the value of entropy and other important parameters of a system in terms of easily measurable quantities. The Maxwell's relations can be obtained by different mathematical methods. However, they may also be obtained with the help of thermodynamic potentials as given below;

Maxwell's first thermodynamic relation: it can be deduced by using the expressions for the temperature and pressure in terms of internal energy [equation (11.3)] *i.e.*

$$\left(\frac{\partial U}{\partial S}\right)_V = T$$
, and $\left(\frac{\partial U}{\partial V}\right)_S = -p$

As dU is an exact differential, so, we can write;

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

$$\left(\frac{\partial T}{\partial V} \right)_{S} = -\left(\frac{\partial p}{\partial S} \right)_{V}$$
(11.17)

or

Equation (11.17) is known as Maxwell's first relation.

<u>Maxwell's second thermodynamic relation</u>: It can be deduced by using the expressions for the pressure and entropy in terms of Helmholtz function [equation (11.12)] *i.e.*

$$\left(\frac{\partial F}{\partial V}\right)_T = -p$$
, and $\left(\frac{\partial F}{\partial T}\right)_V = -S$

Being an exact differential, we can write for Helmholtz function as;

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

or

$$\left(\frac{\partial p}{\partial T}\right)_{V} = \left(\frac{\partial S}{\partial V}\right)_{T} \tag{11.18}$$

Equation (11.17) is known as Maxwell's second relation.

<u>Maxwell's third thermodynamic relation:</u> It can be deduced by using the expressions for the temperature and volume in terms of enthalpy [equation (11.9)] *i.e.*

$$\left(\frac{\partial H}{\partial S}\right)_p = T$$
, and $\left(\frac{\partial H}{\partial p}\right)_V = V$

As dH is an exact differential, we may write;

$$\frac{\partial}{\partial p} \left(\frac{\partial H}{\partial S} \right)_p = \frac{\partial}{\partial S} \left(\frac{\partial H}{\partial p} \right)_V$$

or

$$\left(\frac{\partial T}{\partial p}\right)_{S} = \left(\frac{\partial V}{\partial S}\right)_{p} \tag{11.19}$$

which is the Maxwell's third relation.

<u>Maxwell's fourth thermodynamic relation</u>: It can be deduced by using the expressions for the entropy and volume in terms of Gibbs function [equation (11.16)] *i.e.*

$$\left(\frac{\partial G}{\partial T}\right)_p = -S, and \left(\frac{\partial G}{\partial p}\right)_V = -V$$

dG isan exact differential and hence we can have;

$$\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial T} \right)_T = \frac{\partial}{\partial T} \left(\frac{\partial G}{\partial p} \right)_V$$

or

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \tag{11.20}$$

which is the Maxwell's fourth relation.

11.7The concept of availability: Obtaining equilibrium

Keeping into the mind the inequality in the entropy change of a thermodynamic system, we define quantity'availability':

$$A = U + p_0 V - T_0 S (11.21)$$

It is very helpful in understanding about how systems may bring to their equilibrium statesplaced in contact with the surroundings. Consider a system in contact with surroundings which are at pressure p_0 and temperature T_0 . Let we transfer energy dU and volume dV from the surroundings, to the system. If the change in the internal energy of the surroundings, in this way, be dU_0 , then we can write:

$$dU_0 = -dU = T_0 dS_0 - p_0 \left(-\frac{dV}{}\right) \tag{11.22}$$

Here, (-) sign indicates the fact that the energy and volume in the surroundings are decreasing. We can rewrite equation (11.22) by re-arranging the terms as:

$$dS_0 = -\left[\frac{dU + p_0 \, dV}{T_0}\right] \tag{11.23}$$

where dS_0 expresses the change in the entropy of the surroundings. Now, if the change in the entropy of the system be dS_7 ; then net change in the entropy of the universe dS_{Total} will equal to the sum of dS_0 and dS_1 .e.

$$dS_{Total} = dS_0 + dS (11.24)$$

And, with the fact given by second law of thermodynamics i.e. $dS_{Total} \ge 0$, we have;

$$dS_{Total} = dS - \left[\frac{dU + p_0 \, dV}{T_0}\right] \ge 0$$

$$or T_0 dS_{Total} = -[dU + p_0 dV - T_0 dS] \ge 0$$

or
$$dA = dU + p_0 dV - T_0 dS \le 0$$

or $dA \leq 0$ (p_0 and T_0 being constants) (11.25)

where $A = U + p_0 V - T_0 S$ is termed as availability. It is clear from equation (11.25) that the changes in $\bf A$ are always negative. As a system settles down to equilibrium, any changes will always force $\bf A$ to decrease and it becomes constant at equilibrium. So, to achieve equilibrium, $\bf A$ has to be minimized. However, the kind of equilibrium achieved depends on the nature of the constraints which is discussed below;

System with fixed entropy and volume:

For a system with fixed entropy and volume, we have dS = dV = 0, and hence equations (11.21) and (11.25) imply that:

$$dA = dU \le 0 \tag{11.26}$$

So, to obtain the equilibrium state for such a system, we must minimize U

System with fixed entropy and pressure:

In this case dS = dp = 0, and hence equations (11.21) and (11.25) imply that:

$$dA = dU + p_0 dV \le 0$$

Now, with the definition of enthalpy *i.e.* dH = dU + pdV + Vdp and the systems constraints $p = p_0$ (which implies dp = 0), we have that

$$dH = dU + p_0 dV$$

And hence

$$dA = dH \le 0 \tag{11.27}$$

So, enthalpy must be minimized to find the equilibrium state.

System with fixed volume and thermally isolated:

For thermally isolated systems no heat transfer takes place between system and its surroundings (dQ = 0) and due to fixed volume in this case, system will do no work(dV = 0). This implies dU = 0 and hence from equation (11.25):

$$dA = -T_0 dS \le 0$$

or
$$dS \ge 0$$

Thus we must maximize entropy to get equilibrium state.

System at constant temperature and having fixed volume:

In this case dT = 0 and dV = 0, and hence from the expression $dA = dU + p_0 dV - T_0 dS \le 0$,

$$dU - T_0 dS \le 0 \tag{11.28}$$

And, from the definition of Helmholtz function: F = U - TS, we may write;

$$dF = dU - T_0 dS - S dT$$
or
$$dF = dU - T_0 dS (as dT = 0)$$

So that the condition given by equation (11.28) can be written as;

$$dF \le 0 \tag{11.29}$$

This implies that Helmholtz function must be minimized to get the equilibrium.

System at constant temperature and pressure:

Let us start with the definition of Gibbs function: G = H - TS

or
$$dG = dH - TdS - SdT$$

or $dG = dU + p_0 dV + Vdp - T_0 dS - SdT$

But for the system at constant temperature and pressure (i. e. dT = dp = 0),

$$dG = dU - T_0 dS + p_0 dV$$
or
$$dG = dU - T_0 dS + p_0 dV = dA$$

And hence the condition of minimized availability for such system can be written as;

$$dG \le 0 \tag{11.30}$$

Clearly, the equilibrium state for such system can be obtained by minimizing G.

11.8 Summary

- The combinations of state variables and internal energy such as U, U + pV = H, U TS = F, and H TS = G are called as thermodynamic potentials.
- Like internal energy U, enthalpy (H), Helmholtz function (F), and Gibbs function (G) are state functions and hence are exact differentials.
- The differentials of the thermodynamic potentials is expressed as;

$$dU = TdS - pdV$$

$$dH = TdS + Vdp$$

$$dF = -SdT - pdV$$

$$dG = -SdT + Vdp$$

• Maxwell's relation can directly be deduced using thermodynamic potentials. The relations are;

$$\left(\frac{\partial T}{\partial V}\right)_{S} = -\left(\frac{\partial p}{\partial S}\right)_{V} \quad (first \ relation)$$

$$\left(\frac{\partial p}{\partial T}\right)_{V} = \left(\frac{\partial S}{\partial V}\right)_{T} \quad (second\ relation)$$

$$\left(\frac{\partial T}{\partial p}\right)_{S} = \left(\frac{\partial V}{\partial S}\right)_{p} \qquad (third\ relation)$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \qquad (fourth\ relation)$$

The availability can be defined as:

$$A = U + p_0 V - T_0 S$$

- The conditions to find the equilibrium state of a system is; $dA \le 0$ Which means, for a system in contact with a reservoir (temperature T_0 and pressure p_0), the equilibrium state can be obtained by:
 - ✓ Minimizing U when S and V are fixed;
 - ✓ Minimizing H when S and p are fixed;
 - ✓ Minimizing F when T and V are fixed;
 - ✓ Minimizing G when T and p are fixed;

11.9 Exercises

Subjective questions:

- [1] What are the thermodynamic potentials? Why are they called potentials?
- [2] Write down the physical significance of thermodynamic potentials.
- [3] What are natural variables? Express the differentials of thermodynamic potentials in terms of their natural variables.
- [4] Deduce Maxwell's relations using thermodynamic potentials.
- [5] Prove that:

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

(ii) $C_P = \left(\frac{\partial H}{\partial T}\right)_P$

[6] Derive the following relations;

$$(i) \left(\frac{\partial T}{\partial V} \right)_{U} = -\frac{1}{C_{V}} \left[T \left(\frac{\partial p}{\partial T} \right)_{V} - p \right]$$

$$(ii) \left(\frac{\partial T}{\partial V}\right)_{S} = -\frac{1}{C_{V}} T \left(\frac{\partial p}{\partial T}\right)_{V}$$

$$(iii) \left(\frac{\partial T}{\partial V} \right)_{U} = -\frac{1}{C_{p}} \left[T \left(\frac{\partial V}{\partial T} \right)_{p} - V \right]$$

[7] What is availability? Write down its significance.

Short answer type questions:

- 1 Prove that isothermal process for ideal gas is iso-enthalpic too.
- 2 Prove that change in enthalpy in an isobaric process is equal to the heat transferred.
- 3 Prove that change (decrease) in the Helmholtz function in an isothermal process is equal to the work done by the system.
- 4 Prove that for a reversible isothermal and isobaric process, Gibbs function remain
- 5 Show that one has to minimize Helmholtz function to find the equilibrium of a system at constant temperature and volume.
- 6 Show that Helmholtz free energy never increases in natural processes.

Objective questions:

- Thermodynamic potentials are; 1
 - (a) P, V, T S
 - (b) U, F, G, H
 - (c) S, F, H, G
 - (d) S, U, H, G
- Which statement is wrong concerning thermodynamic potentials;
 - (a) These are functions of sate variables p, V, T and S
 - (b) These are exact differentials
 - (c) Not all the potentials are state functions
 - (d) These are extensive quantities of a system.
- Which is a write equation;
 - (a) dU = TdS + pdV
 - (b) dU = SdT + pdV
 - (c) dU = TdS pdV
 - (d) dU = TdS Vdp
- 4 Which is a wrong equation;
 - (a) F = U TS
 - (b) H = U + pV
 - (c) G = F + pV
 - (d) G = H + TS
- 5 Which is not a Maxwell's relation;

 - (a) $\begin{pmatrix} \frac{\partial T}{\partial V} \\ S \end{pmatrix}_S = -\begin{pmatrix} \frac{\partial p}{\partial S} \\ \frac{\partial P}{\partial S} \end{pmatrix}_V$ (b) $\begin{pmatrix} \frac{\partial p}{\partial T} \\ V \end{pmatrix}_V = \begin{pmatrix} \frac{\partial S}{\partial V} \\ \frac{\partial P}{\partial T} \end{pmatrix}_T$ (c) $\begin{pmatrix} \frac{\partial S}{\partial p} \\ \frac{\partial S}{\partial T} \end{pmatrix}_V = -\begin{pmatrix} \frac{\partial P}{\partial S} \\ \frac{\partial S}{\partial T} \end{pmatrix}_T$

- 6 Which is a wrong statement;
 - (a) In an isothermal change of a mechanically isolated system, H remains constant
 - (b) Gibbs free energy always increases in natural processes
 - (c) G do not change in a reversible isothermal and isobaric process
 - (d) Helmholtz free energy never increases in natural processes

11.9 Glossary

Exact differentials: A differential dF is said to be exact if:

- The function F exists; and
- \rightarrow $\int_i^f dF = F(f) F(i)$ is independent of the path followed.

Natural variables: The thermodynamic parameters or variables that are held constant in the process are termed the natural variables of that potential. These are of great importance as if a thermodynamic potential can be determined as a function of its natural variables, all of the thermodynamic properties of the system can be found by taking partial derivatives of that potential with respect to its natural variables.

Isobaric processes:The processes during which the pressure is kept constant *e.g.* melting of ice in air (the pressure i.e. atmospheric remains constant).

Isochoric processes: The process during which the volume is kept constant *e.g.* heating or the cooling of the contents of a sealed, inelastic container is an isochoric or an isovolumetric or an isometric process.

Isentropic processes:The process during which the entropy is kept constant *e.g.* any reversibleadiabatic process is an isentropic process.

Isenthalpic processes:The process during which the enthalpy is kept constant *e.g.*the throttling process is a good example of an isenthalpic process.

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