Thermodynamic Potentials and Thermodynamic Parameters

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ABSTRACT

The concept of thermodynamic potentials was introduced by Pierre Duhem in 1886. These potentials have been derived from the concept of potential energy. These potentials deal with mechanical work, non-mechanical work, heat added and heat released from a thermodynamic system. Four thermodynamic potentials are internal energy, the enthalpy, the Helmholtz free energy and the Gibbs free energy. All the thermodynamic potentials are energy terms. These potentials cannot be measured like temperature or pressure. These can be found from the measurable variables like pressure, volume and temperature. These involve the terms +p V and –TS. All the thermodynamic properties of a system can be found by taking the partial derivatives of the thermodynamic potentials. Thermodynamic potentials have multiple independent variables associated. Second order partial differentials of a thermodynamic potential with respect to natural variables is independent of the order of differentiation (\(\frac{\partial^2 P}{\partial x \partial y} = \frac{\partial^2 P}{\partial y \partial x}\)). There are ten thermodynamic parameters which are used for the performance analysis of power producing as well as power consuming thermodynamic machines and devices. These are also employed to compare different thermodynamic cycles for their power input and efficiency. Proper selection of the transport properties reduce the pressure drop, power input and the running cost. Study of thermodynamic potentials as well as thermodynamic parameters is extremely useful to the students, teachers, researchers, consultants and the persons in the industry.

Keywords--- Thermodynamic Potential, Thermodynamic parameters, internal energy Enthalpy, Entropy, Gibbs Potential, Pressure-Enthalpy chart

I. INTRODUCTION

Thermodynamics is one of the most important subjects of Mechanical Engineering. It deals with the change of one form of energy into another form. It is mostly change of heat to work in all power producing devices like petrol, diesel, steam engines and steam, gas and water turbines. In a water turbine, it is change of potential energy into kinetic energy and as such no conversion of heat into work. It also includes change of work to heat in all power consuming devices like refrigerating and air conditioning machinery, compressors, pumps, fans and blowers. Here too in case of pumps and blowers there is no conversion of work into heat. It is difficult to understand thermodynamics without learning the thermodynamic potentials and thermodynamic parameters. These are dealt in a simple manner in this paper. There are four thermodynamic potentials namely internal energy, the enthalpy, the Helmholtz free energy and the Gibbs free energy. Their partial derivatives help to find the various thermodynamic properties. Thermodynamic parameters help to analyze the performance of power producing engines and turbines as well power consuming devices like compressors, pumps, blowers and fans. [1-5]

II. THERMODYNAMIC POTENTIALS

A thermodynamic potential is a scalar quantity. It represents the thermodynamic state of a system. The concept of thermodynamic potentials was introduced by Pierre Duhem in 1886. Josiah Willard Gibbs called these as fundamental functions. These potentials have been derived from the concept of potential energy. It is well known that potential energy is the capacity to do work. Similarly internal energy (U) is the capacity to do useful work plus the capacity to release heat energy. Enthalpy (H) is the capacity to do non- mechanical work plus the heat energy given to the system. Non mechanical work means like chemical energy/electrical energy/thermal energy/acoustic energy/nuclear energy/radiant energy. These are not due to position or motion of a body i.e. these are other forms of energy. Helmholtz energy (F) is the capacity to do reversible work or useful work (mechanical work). Gibbs energy (G) is the capacity to do non- mechanical work. From the above, it can be easily concluded that if \(\Delta U\) is the energy added to a system, \(\Delta F\) is the total work done, \(\Delta G\) is
the non-mechanical work done while ΔH is the sum of non-mechanical work done and the heat given to it. [2-7]

Thermodynamic potentials are useful in the thermodynamics of chemical reactions. These potentials also describe the non-cyclic processes. They are four thermodynamic potentials as mentioned in Table1. These are internal energy, the enthalpy, the Helmholtz free energy and the Gibbs free energy. All the thermodynamic potentials are energy terms. These potentials cannot be measured like temperature or pressure. These can be found from the measurable variables like pressure, volume and temperature as mentioned in Table 2. Thermodynamic potentials, fundamental equation and equilibrium conditions are mentioned in Table 3. These involve the terms +p V and –TS. All the thermodynamic properties of a system can be found by taking the partial derivatives of the thermodynamic potentials as given below:

\[ \frac{\partial U}{\partial T}V = T \]
\[ \frac{\partial F}{\partial P}T = -P \]
\[ \frac{\partial G}{\partial V}T = V \]

Further ΔF is the measure of useful work under constant temperature (T) and constant volume (V). ΔG is the useful work done under constant temperature (T) and constant pressure (P).

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>Therodynamic potential</th>
<th>Natural variables (which are kept constant in the process)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>U</td>
<td>S, V</td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>S, p</td>
</tr>
<tr>
<td>3</td>
<td>G</td>
<td>T, p</td>
</tr>
<tr>
<td>4</td>
<td>F</td>
<td>T, V</td>
</tr>
</tbody>
</table>

These thermodynamic potentials are connected with experimentally measureable thermodynamic parameters and thus make their estimations indirectly. It is noticeable that thermodynamic potentials have multiple independent variables. There is an important feature of all the multiple variable functions that the mixed partial derivatives do not depend on the order in which these are used like

\[ \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \] (It is Euler’s Reciprocity Law of thermodynamics)

III. NATURAL VARIABLES

The variables which are kept constant in a process are called the natural variables of that potential. Thermodynamic potential can be found as a function of its natural variables only. Then only the thermodynamic properties of the system can be determined by taking partial derivatives of that potential with respect to its natural variables. If the thermodynamic potential is not known in terms of its natural variables, then thermodynamic properties cannot be found from the partial derivatives of that potential.

Natural variables for the four thermodynamic potentials are formed from every combination of the T-S and P-V variables, excluding any pairs of conjugate variables. The conjugate pairs are made with \( \mu_i \) and \( N_i \).

Where \( \mu_i \) is the chemical potential for an i-type particle. \( N_i \) is the number of particles of type i in the system.

IV. MAXWELL RELATIONS

These are based on the fact that second order partial differentials of a thermodynamic potential with respect to natural variables is independent of the order of differentiation. T and S are thermal natural variables and p and v are mechanical natural variables. The Maxwell relations were first derived by James Clerk Maxwell. These equations are derived by application of Euler's reciprocity relation to the thermodynamic potentials given below:
\[ \frac{\partial^2 P}{\partial x \partial y} = \frac{\partial^2 P}{\partial y \partial x} \]  (Euler's reciprocity relation)

The four most common Maxwell equations are
\[ dU = T \, dS - P \, dV = + (\frac{\partial S}{\partial P} \partial V) \]
\[ dH = S \, dT + P \, dV = + (\frac{\partial S}{\partial V} \partial P) \]
\[ dF = T \, dS - P \, dV = + (\frac{\partial S}{\partial V} \partial P) \]
\[ dG = T \, dS + P \, dV = - (\frac{\partial S}{\partial T} \partial P) \]

Hence various thermodynamic potentials can be found by using second order partial differential equations and the measureable thermodynamic parameters.

**Exact differentials in thermodynamics are written as**
- \( \delta U \), \( \delta W \), \( \delta Q \)

Non exact differentials in thermodynamics are written as
- \( dU \), \( dQ \), \( dW \)

Use of exact and non exact differentials

(i) \( dU = \delta Q - \delta W + \) Chemical potential---applicable for a non-reversible change

(ii) \( \delta Q = T \, dS \)---only for a reversible process

(iii) \( \delta W = P \, dV \)--- only for a reversible process

**V. THERMODYNAMIC PARAMETERS**

i. Principle of Maximum Entropy and that of Minimum Energy are equivalent.

ii. Laws of Thermodynamics

iii. Datum in Thermodynamics

iv. Thermodynamic Temperature

v. Thermodynamic Scale

vi. Thermodynamic Properties

vii. Transport Properties

viii. Temperature Entropy Chart

ix. Pressure Enthalpy Chart

x. Availability, Unavailability And Irreversibility [1-7]

**i) Principle of Maximum Entropy and that of Minimum Energy are equivalent**

Principle of Maximum Entropy: Any thermodynamic system comes in equilibrium as soon as the entropy of the system becomes maximum for the given value of total internal energy.

Principle of Minimum Energy: Any thermodynamic system comes in equilibrium as soon as the energy of the system becomes minimum for the given value of total entropy.

**ii) Laws of Thermodynamics**

(a) Zeroth law explains thermal equilibrium which necessary for the measurement of temperature in the system. It is a prerequisite for the 1st, 2nd and 3rd laws of thermodynamics.

(b) First law is law of conservation of energy. It gives the definition of the internal energy. The internal energy is the difference of heat supplied minus work obtained from the system. It will increase in power producing devices and will decrease in power consuming devices.

(c) Second law is the law of irreversibility. Definition of entropy comes from this law as increase of entropy in any process is measurement of irreversibility. Every natural process is irreversible and hence results in increase of entropy. Thus the entropy of the universe is increasing.

(d) Third law of thermodynamics gives the measurement of entropy. Entropy decreases with the decrease of temperature. It becomes zero at absolute zero i.e. at -2730C.

**ii) Datum in thermodynamics**

Thermodynamics deals with energy conversion from one form to another. For doing such conversion, it requires a fluid as a working substance. When the working substance is a vapor as in steam engines and refrigeration systems, the working equations are highly complex and cumbersome. Therefore in such cases, datum level is used to create tabular and graphical data for determining the performance of systems using vapors. Datum levels used in ISI units are as given below:

(a) For Refrigeration Systems

Datum is -400C
Entropy = 0
Enthalpy = 0

(b) For steam systems

Datum level is 00C.
Entropy = 0

(C) For gases

No datum for gases since various simple gas laws is applicable.

**iv) Thermodynamic temperature**

Temperature is due to the random translation, rotational motions and vibrations of the submicroscopic particle constituents of matter. These motions constitute the internal energy of a substance. Thermodynamic temperature is the measure of the average kinetic energy per degree of freedom of its constituent particles and it is ABSOLUTE and it is one of the important thermodynamic parameters. Kinetic energy is considered zero at absolute zero which is also called the Null point. Third law of thermodynamics defines the thermodynamic temperature. Lowest thermodynamic temperature is the absolute zero. Temperature cannot go below this temperature because at this temperature the particle constituents of matter have minimal motion. Zero absolute temperature has also been called the ground state of matter. At this, matter is in its state of minimum energy level. Thermodynamic temperature has been called absolute temperature because of being proposed by Kelvin.
and this also does not depend on the properties of the working medium.

v) Thermodynamic temperature scale

All other scales of temperature are dependent on the properties of the working substance. While thermodynamic temperature scale is independent of the working medium. It is based on the fact the efficiency of a reversible steam engine depends only on two temperatures and not on the properties of the working substance. Thermodynamic scale differs from empirical scales in that it is absolute. It is based on basic laws of thermodynamics. Thermodynamic scale is based on the efficiency of the reversible heat engines. Absolute thermodynamic temperature scale is developed from the second law of thermodynamics. The International System of Units has defined a scale for the thermodynamic temperature. It has been called the thermodynamic temperature scale. Its lower limit is absolute zero (0 K) or (-273°C) and upper point is the triple point of water at 273.16K or 0.16°C.

(a) Salient Features Of The Thermodynamic Temperature Scale

1) One Kelvin is 1/273.16 of difference between absolute zero and the triple point of water
2) It fixes one Kelvin equal to 10C.
3) Thermodynamic temperature scale covers temperatures only between absolute zero (0 K) and the triple point of water (273.16 K and 0.01 °C).
4) For temperature outside this range, many different thermometer designs are required to cover the entire range. Such thermometers are helium vapor pressure thermometers, helium gas thermometers, standard platinum resistance thermometers, monochromatic radiation thermometers and liquid (mercury) thermometers.

(b) Different Temperature Scales

1) Empirical Temperature Scale -- Celsius, Kelvin, Fahrenheit etc...
2) Ideal Temperature Scale -- Thermodynamic Temperature Scale and International Temperature Scale

(c) Practical Applications of Thermodynamic Temperature

Normally temperature (°C, °F etc.) is not used in thermodynamics. Temperature is used only in equations involving temperature difference. Thermodynamic temperature is most convenient in all the equations used in thermodynamics. Boyle’s Law, Charles Law, Perfect gas equation etc. all use thermodynamic temperature i.e. absolute temperature. It is also used in finding the efficiency of Carnot heat engine, COP of a Reversed Carnot cycle refrigerator as well as that of a heat pump.

vi) Thermodynamic properties

(a) Fundamental Thermodynamic Properties--Three

Measureable properties like temperature, pressure and volume are the three fundamental thermodynamic properties.

(b) Derived Thermodynamic Properties—Three

Non measureable properties like internal energy, enthalpy and entropy are called derived thermodynamic properties. Definition of internal energy comes from the first law of thermodynamics. Definition of entropy comes from the second law of thermodynamics. Measurement of entropy comes from the third law of thermodynamics. Definition of enthalpy comes from the total heat content which the sum of internal energy and the flow work.

(i) Internal energy

Internal Energy (invisible energy), U, is the sum of kinetic and potential energy of the random translational, rotational and vibratory motion of the atoms or molecules of the system. It also includes the any potential energy due to the bonding the particles together. It is represented by u for 1 kg mass and U for m kg mass. Its units are KJ. From the First Law of Thermodynamics, it is very clear that the internal energy of a system can be increased with rise of temperature on adding energy to the system or by doing work on the system.

\[ U = Q - W \]  

(ii) Entropy

Entropy is measure of disorder. More is the disorder, more will be entropy. Entropy can also be said as incomplete information about the system because it is a disorder. Mathematically \( \delta V / V \) is a measure of disorder. It will increase in an expansion process and vice versa. Only difference of entropy is defined as its values have been taken as zero with respect to a datum. Thus it cannot have an absolute value. Entropy of water is taken as zero at 00C and then values of entropy have been tabulated in steam tables. Similar is the case of refrigerants. Entropy of each refrigerant has been taken as zero at ~400C in S.I. Units. Entropy values at other temperatures have been tabulated. Temperature-entropy charts have also been prepared from the tabulated data. Units of specific entropy and total entropy are kJ / kg K and kJ/K respectively. However specific entropy (kJ / kg K) is in maximum use.

(iii) Enthalpy

It is sum of internal energy and flow work. Mathematically 

\[ h = u + PV \]

vii. Transport properties--three

These include the specific heat, viscosity and thermal conductivity.

(a) Specific heats

There can be three values of Cp and three values of Cv depending upon whether the gas is mono-atomic, diatomic or polyatomic as given in Table 4. As per Equi-partition theorem, energy is equally distributed for each degree of freedom by the amount \( RT / 2 \) (J/mol). R is universal gas constant, T is the absolute temperature. A
mono-atomic gas has only three degrees of translational motion. A diatomic gas has three degrees of translational motion and two degrees of rotational motion. A polyatomic gas has three degrees of translational motion as well as three degrees of rotational motion.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mono-atomic</th>
<th>Diatomic</th>
<th>Polyatomic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degrees of freedom=</td>
<td>3+0 = 3</td>
<td>3+2=5</td>
<td>3+3 = 6</td>
</tr>
<tr>
<td>Trans + Rotational</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_v$</td>
<td>$3RT/2$</td>
<td>$5RT/2$</td>
<td>$6RT/2$</td>
</tr>
<tr>
<td>$c_p$</td>
<td>$5RT/2$</td>
<td>$7RT/2$</td>
<td>$8RT/2$</td>
</tr>
</tbody>
</table>

It is important to understand that vibration modes have been neglected since these are found only at very high temperature which is not found in day to day applications. Values have been tabulated at 20°C or 293 K.

(b) Viscosity

The working substance in thermodynamics is mostly gas and vapor. Liquid is in very limited use. Therefore, it is important to discuss the viscosity. Viscosity is the friction between adjacent layers of liquids, vapors and gases and is governed by Newton’s Law of Viscosity. Viscosity is the resistance to flow of a fluid. It is the internal fluid friction (shear force) between any two adjacent moving layers of a fluid. It is due to Cohesion and momentum transfer between adjacent layers.

Dynamic viscosity ($\mu$, units are Ns/m$^2$) and kinematic viscosity ($\nu = \mu/\rho = m^2/s$)

Viscosity of liquids decrease with the increase of temperature and vice versa. There is no effect of pressure on the viscosity of liquids. Viscosity of gases increase with the increase of temperature and vice versa. Viscosity of gases is also affected by pressure.

Viscosity in general is governed by Newton’s Law of Viscosity. Mathematically

$$\dot{z} = \mu \frac{du}{dy}$$

Where $\dot{z}$ is the shear stress (N/m$^2$)

$du$ change in velocity in x direction (direction of motion) in m/s

dy is the distance (perpendicular to $du$) between the two layers in y direction, m

$\mu$ is constant of proportionality and is called dynamic viscosity (Ns/m$^2$).

(c) Thermal Conductivity

It depends upon density, temperature and pressure in case of gases while for liquids it depends only upon temperature since the density of liquids is constant at any temperature and pressure. High density means high thermal conductivity. Rise of temperature increases the thermal conductivities of liquids and gases and vice versa. Increase of pressure decreases the thermal conductivity of gases and vice versa. However thermal conductivity of a liquid is unaffected by the change of pressure.

viii. Temperature Entropy Chart

Entropy is a thermodynamic parameter (property) like other thermodynamic parameters namely internal energy/enthalpy. Absolute temperature is the ordinate. Entropy is used as abscissa (x -co-ordinate). This chart (Fig.1) is very useful in comparing the performance of various heat engine and refrigeration cycles. It is specifically useful for analysis when tabular data is available. As such, temperature entropy charts are not available except for permanent gases like air, oxygen, nitrogen, hydrogen and helium. These charts for permanent gases are useful for finding percentage yields on liquefaction. Although entropy is an extensive (depends on mass) thermodynamic property and its concept comes from the second law of thermodynamics (Clausius inequality). Conventionally it is in maximum use as an intensive property in kJ/kg K in the analysis of various cycles.

\[\text{Fig.1 Temperature Entropy Chart}\]

- Constant Pressure Line is ABCD.
- Another Constant Pressure Line is EFGH
- Constant temperature Line is Horizontal.
- Constant Entropy Line is Vertical. Area on this diagram is heat quantity.

ix. Pressure Enthalpy Chart
Fig. 2 Pressure Enthalpy chart

P-h chart contains

These charts (Fig. 2) are used for analyzing the performance of machines operating with vapors such as refrigeration and air conditioning plants.

a. Isothermal line
   - Vertical in sub-cooled region
   - Horizontal in two-phase region
   - Curve like in super-heated region
   - FGHI is Constant Temperature Line
   - JKLM is another Constant Temperature Line

b. Constant pressure lines—Horizontal Lines

c. Constant specific entropy lines—more inclined to horizontal and are plotted in the super-heated region. NO and PQ are Constant Entropy Lines

d. Constant specific volume lines—less inclined to horizontal and are plotted in the super-heated region. RS and TU are Constant Specific Volume Lines.

e. Constant Enthalpy Lines—Vertical Lines are Constant Enthalpy Lines.

f. Saturated Liquid Line—Curve ABC is saturated liquid line.

g. Saturated vapor Line—Curve CDE is the saturated vapor line.

h. Sub-cooled region—towards left of saturated liquid line.

i. Two-phase region—in between saturated liquid line and dry saturated vapor line

j. Super-heated region—towards right of dry saturated vapor line

k. Gaseous region—towards right of saturated vapor region where degree of super-heat is > 50°C

x. Availability, Unavailability and Irreversibility

(a) Available Energy

Available energy is related to the energy grade. There are two grades of energy available from the various sources.[8]

(i) High Grade Energy—can be fully converted useful work (Shaft Work) and is not governed by the Second Law of Thermodynamics (no irreversibility). Examples of high grade energy are Mechanical work, Electrical energy, Potential energy, Kinetic energy, wind power, water power, Jet energy and Tidal energy.

(ii) Low-grade energy—Cannot be fully converted useful work (Shaft Work) and is governed by the Second Law of Thermodynamics. Examples of low grade energy are heat from nuclear fission or fusion, heat from combustion of fossil fuels, solar energy and heat energy from any other source.

The high-grade energy is obtained from low-grade energy. The complete conversion of low grade energy into high grade (shaft work) is impossible. Thus the available energy is the amount of low-grade energy which can be converted into high grade energy.

(b) Unavailable Energy

The amount of low-grade energy which cannot be converted into high grade energy is unavailable energy.

(c) Irreversibility

It is the difference of available energy and the useful work obtained.

(d) Theoretical Available Energy between Two Reservoirs

(i) First reservoir at constant temperature but at a higher temperature than the atmospheric temperature
(ii) Second reservoir is at constant atmospheric temperature

(e) Theoretical Available Energy

It is the amount of useful work which will be available up to atmospheric temperature and pressure as no energy can be converted into useful work below the atmospheric conditions.

(f) Theoretical Unavailable Energy

It is equal to the product of atmospheric temperature (or lowest temperature of heat rejection) and the change of entropy of the system during the process of work conversion.

(g) Theoretical Available Energy between Two Finite Sources

Finite source is one where temperature is variable. With the same starting temperatures of finite sources, availability will be less as compared with the case of two reservoirs.

VI. CONCLUSIONS

(i) Thermodynamics and its applications can be best understood with the help of thermodynamic potentials and thermodynamic parameters.

(ii) It will be truly applicable both for power producing devices (like internal combustion engines, external combustion engines, steam, water and gas turbines) as well as power consuming devices like refrigeration and air conditioning plants, compressors, motors, pumps, fans and blowers.

(iii) One will be able to make improvements in the various machines to increase their efficiency as well as other operating performance.
(iv) Power will be saved in power consuming machines and more power will be produced by power producing devices.
(v) All the devices will become more cost effective and environment friendly.

REFERENCES

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